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Division of Chemical Science

(IZVESTIYA AKADEMY NAUK SSSR)

(OTDELENIE KHIMICHESKIKH)

IN ENGLISH TRANSLATION

1957 NO. 8

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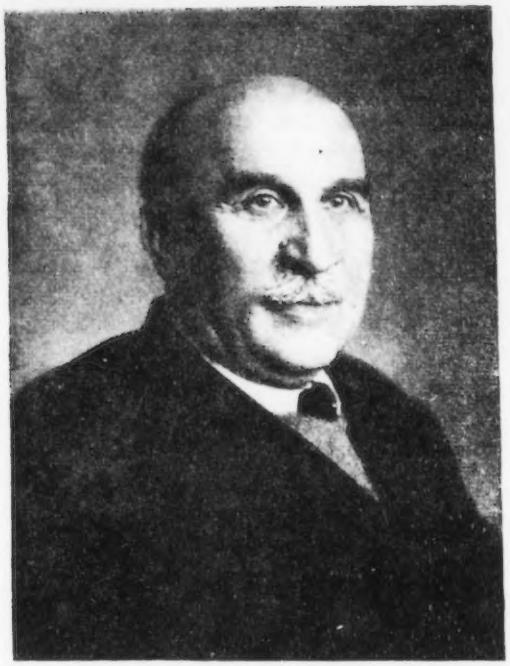
SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.–Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. – Publisher.



GEORGY GRIGORYEVICH URAZOV

(Obituary)

The eminent chemist and metallurgist Academician Georgy Grigoryevich Urazov died on April 27, 1957.

G. G. Urazov headed the well known Soviet school of physicochemical analysis founded by Academician N. S. Kurnakov. Dozens of investigators were brought together under his leadership and in collaboration with them he creatively developed the theory and experimental methods of physicochemical analysis and also contributed in many ways to the advancement of our knowledge of the nature of alloys, salt systems, minerals, and of other fields of great scientific and industrial importance.

After graduation at the Petrograd (now Leningrad) Polytechnical Institute in 1909, Urazov, in addition to teaching activities, undertook research work under N. S. Kurnakov, first in the Polytechnical Institute, and then in the Institute of Physicochemical Analysis of the Academy of Sciences of the USSR, which was founded in 1918. In 1939 he was elected Corresponding Member of the Academy of Sciences, and in 1946 he was elected Academician.

Urazov published more than 180 scientific works relating to investigations on alloys, sulfides, chlorides, metal ores and methods for their treatment, aqueous salt equilibria, and natural salts. Everyone is acquanted with the classical work of Urazov and his students on the investigation and treatment of bauxite ores, which was of great importance for the creation of the Soviet aluminum industry. Urazov's investigations on the elucidation of the physicochemical nature of alloys of aluminum with magnesium, copper, silicon, and other elements provided the scientific basis for the manufacture of high-strength alloys. Urazov was one of the pioneers in the development and application of the method of chlorination and treatment of metal ores containing rare metals of great potential importance in industry.

Throughout the many years of his scientific activities, Urazov gave much attention to the physicochemical study of the mineral-salt wealth of the country and its industrial utilization: he carried out work on the elucidation of the origin of the Solikamsk potassium salts and investigated the borax waters and salt lakes of the North Caucasus and the salt deposits of the Caspian and Volga regions. In recent years Urazov has given particular attention to the very large salt basin of the Kara-Bogaz-Gol Gulf. The work of Urazov and his students in this field was of

great importance for the founding of the Soviet iodine, bromine, potash, and sulfate industries.

During the many years that have elapsed since Kurnakov's death, Urazov has been Director of the Physicochemical Analysis Section of the N. S. Kurnakov Institute of General and Inorganic Chemistry of the Academy of Sciences of the USSR. Urazov devoted much attention to the training of chemical and metallurgical scientific staff: for some years he was Director of the Department of the Technology of Fine Inorganic Products in the Moscow Institute of Fine Chemical Technology and Director of the Department of the Metallurgy of Heavy Nonferrous Metals in the M. I. Kalinin Institute of Nonferrous Metals and Gold, Moscow.

For his outstanding services to Soviet chemistry, to nonferrous metallurgy, and in the training of scientific staff, the government awarded him two Orders of Lenin, the Order of the Red Banner of Labor, the Order of the Red Star, the Badge of Honor, and various medals.

The memory of this outstanding scientist and sympathetic man will forever remain dear to Soviet chemists and metallurgists.

FORM OF LIQUIDUS CURVES OF BINARY SYSTEMS

COMMUNICATION 1. SYSTEMS OF THE EUTECTIC TYPE WITH NONDISSOCIATING COMPONENTS

Yu. M. Kessler

The question of the factors determining the form of liquidus curves in simple systems is of definite theoretical and practical interest. It would appear that this question was first examined by Van Laar, a statement to this effect being made by Roozeboom in his monograph [1] without any reference to the literature. Roozeboom himself confined himself to a graphical representation of liquidus curves for different values of the entropies of fusion of the components [1]. This question was later examined by various authors [2-5], but in all these studies the form of the liquidus curves was investigated only for ideal systems; moreover, the heats of fusion of the components were assumed to be independent of temperature.

In the present paper the question of the form of liquidus curves is examined for ideal systems, account being taken of the temperature-dependence of the heats of fusion of the components, and for real systems of the eutectic type.

1. Ideal Systems

a) Heats of Fusion of Components are Independent of Temperature, $\Delta H_i \neq f(T)$. Since a mathematically simpler expression for real systems is obtained for $\frac{d^2N_i^*}{dT^2}$, in which N_i is mole fraction, for the sake of uniformity we determined this derivative, and not $\frac{d^2T}{dN_i^2}$ as in [1-5], for ideal systems also. A general way of determining it is differentiation with respect to temperature of the thermodynamic relationship

$$\frac{d\ln N_i}{dT} = \frac{\Delta H_i}{RT^2}; \tag{1}$$

which gives

$$\frac{d^2N_i}{dT^2} = \frac{N_i \Delta H_i \left(\frac{\Delta H_i}{T} - 2R\right)}{R^2T^3}. \tag{2}$$

Substituting T from the equation of Schroeder and le Chatelier

$$\ln N_i = \frac{\Delta H_i}{R}\left(\frac{1}{T_i} - \frac{1}{T}\right), \tag{3}$$

(T_i is the melting point of the i-th component) in Equation (2), we obtain the equation

$$\frac{d^2N_i}{dT^2} = \frac{N_i(\Delta H_i - RT_i \ln N_i)^3}{\Delta H_i^3 \cdot R^2 \cdot T_i^3}\left(\frac{\Delta H_i}{T_i} - R\ln N_i - 2R\right). \tag{4}$$

* Here and in the further treatment differentiation is carried out for P = constant, and for simplicity we write

$$\frac{d^nN_i}{dT^n} \text{ and } \frac{d^na_i}{dT^n} \text{ instead of} \left(\frac{\partial^nN_i}{\partial T^n}\right)_p \text{ and } \left(\frac{\partial^na_i}{\partial T^n}\right)_p.$$

which can be obtained also directly by differentating Equation (3) twice with respect to temperature. The equation for $\frac{d^2T}{dN^2}$, analogous to Equation (4) in the sense of the absolute value of the term $2R - \frac{\Delta H_i}{T_i} + R \ln N_i$ which determines the sign of the second derivative, has been most completely analyzed by Anosov [5]; this sign depends on the relation

$$\frac{\Delta H_i}{T_i} - R \ln N_i \gtrless 2R. \tag{5}$$

We must point out further that as

$$(\Delta S_i)_s = - R \ln N_i, \tag{6}$$

[$(\Delta S_i)_s$ is the change in entropy in the passage of the i-th component from the pure liquid to the solution] and

$$\frac{\Delta H_i}{T_i} = (\Delta S_i)_m, \tag{7}$$

therefore

$$(\Delta S_i)_m + (\Delta S_i)_s = \Delta S_i \gtrless 2R, \tag{8}$$

i.e., for $\Delta H_i \neq f(T)$ the form of the liquidus curves of binary ideal systems depends only on the values of entropy differences associated with the passage of the i-th component from the crystalline state to the solution. The same results follows directly from Equation (2), which may be written in the form

$$\frac{d^2N_i}{dT^2} = \frac{N_i \Delta H_i (\Delta S_i - 2R)}{R^2T^3}. \tag{9}$$

b) Heats of Fusion of Components Are Dependent on Temperature, $\Delta H_i = f(T)$. In this case

$$\frac{d^2N_i}{dT^2} = \frac{N_i \Delta H_i \left(\frac{R\Delta C_p}{\Delta S_i} + \Delta S_i - 2R\right)}{R^2T^3}, \tag{10}$$

and the sign of the second derivative is determined by the relation

$$\frac{R\Delta C_p}{\Delta S_i} + \Delta S_i \gtrless 2R, \tag{11}$$

in which $\Delta C_p = (C_p)_i^l - (C_p)_i^s$. It is easy to see that 1) $R\,\Delta C_p/\Delta S_i$ and ΔS_i are of the same order of magnitude; 2) we may have $\Delta C_p > 0$ and $\Delta C_p < 0$; and for $\Delta C_p = 0$ Equation (10) is converted into (9); 3) the contribution of the term $R\,\Delta C_p/\Delta S_i$ is the greater, the lower ΔS_i. Its neglect, i.e., the assumption of the independence of ΔH_i on temperature, is not permissible in the analysis of the form of liquidus curves, since it leads to incorrect theoretical and practical conclusions. Thus, analyzing his equation, obtained on the assumption that $\Delta H_i \neq f(T)$, on the basis of the view that $(\Delta S_i)_m - R \ln N_i - 2R$ cannot under any conditions be zero in a range of concentrations, so that the second derivative $\frac{d^2T}{dN_i^2}$ also cannot be zero in this concentration range", Anosov [5] concluded that linearity of the liquidus branch of a binary system having a eutectic indicates that the system is nonideal. This conclusion, however, is valid only when $\Delta H_i \neq f(T)$ and cannot be extended, as the author does, to ideal systems in which $\Delta H_i = f(T)$. In fact, since

$$(\Delta S_i)_m^T = (\Delta S_i)_m - \int_T^{T_i} \Delta C_p \, d \ln T, \tag{12}$$

in which $(\Delta S_i)_m^T$ is the change of entropy in the melting of the i-th component at temperature $T < T_i$ in the supercooled liquid and in view of Equations (6) and (8) and the relationship between heat capacity and temperature (11) can be expanded as follows:

$$R\frac{f(T)}{(\Delta S_i)_m-\int_T^{T_i}\Delta C_p\,d\ln T-R\ln N_i}+(\Delta S_i)_m-\int_T^{T_i}\Delta C_p\,d\ln T-$$
$$-R\ln N_i\geqq 2R. \qquad (13)$$

If we denote the left-hand side of this inequality-equality by A, $A \approx 2R$ may be true over a considerable range of concentrations, so that the liquidus branch drawn on the usual scale will be almost linear. For example, for hydrogen sulfide at $T = T_i = 187.63°$ A = 4.07 and at T = 140°K, if $\Delta C_p \neq f(T)$, A = 3.997 (data for $(\Delta S_i)_m$, T_i and ΔC_p are taken from tables [6]), which corresponds to a change in N_i of 17 moles %. This example is a fairly good illustration of the possibility in principle of the equation $\frac{d^2N_i}{dT^2} = 0$ holding over a considerable range of concentrations.

TABLE 1

Substance	$(\Delta S_i)_m$ (entropy units)	ΔC_p (cal/mole · degree)	$\frac{R\Delta C_p}{(\Delta S)_m}$	A	Sign of $\frac{d^2N_i}{dT^2}$		Literature source
					According to [1-5]	According to (10)	
Selenium	2.64	2.2	1.65	4.29	—	+	[6]
Sulfur	0.75	1.6	4.24	4.99	—	+	[6]
Silver chloride	4.36	− 2.31	− 1.05	3.31	+	—	[6]
Carbon tetrachloride	1.88	2.7	2.85	4.73	—	+	[7]
Hexachloroethane	3.71	1.78	0.95	4.66	—	+	[6]
Deuterium	2.5	2.2	1.75	4.25	—	+	[6]
Neon	3.26	2.42	1.47	4.73	—	+	[6]

In some cases the assumption $\Delta H_i \neq f(T)$ made in the papers cited [1-5] results in the sign found for the second derivative being the opposite of that which it actually possesses. This is illustrated by Table 1, which gives values of $(\Delta S_i)_m$, $\frac{R\Delta C_p}{(\Delta S_i)_m}$, ΔC_p and $A = \frac{R\Delta C_p}{(\Delta S_i)_m} + (\Delta S_i)_m$ at $T = T_i$ for several extremely different substances. The last column gives the sources from which values of $(\Delta S_i)_m$ and ΔC_p were taken.

Neglect of the dependence of heat of fusion on temperature therefore leads to erroneous results associated not with neglect of changes of ΔH_i with temperature as compared with the magnitude of ΔH_i itself, but with neglect of an important term in the expression determining the sign and to a considerable extent also the absolute value of the second derivative. When $\Delta H_i = f(T)$, the form of the liquidus curves of binary ideal systems depends not only on the change of entropy in the dissolution of the solid, but also on the ratio of change of heat capacity during dissolution to change of entropy.

2. Real Systems

For real systems Equation (1) becomes

$$\frac{d\ln a_i}{dT}=\frac{\Delta\overline{H}_i}{RT^2}, \qquad (14)$$

in which a_i is the activity of the i-th component in the solution, referred to the pure liquid as the standard state, and $\Delta\overline{H}_i$ is the last heat of solution, i.e., the differential heat of solution in a solution saturated with respect to the i-th component. We then have

$$\frac{d^2a_i}{dT^2}=\frac{a_i\Delta\overline{H}_i\left[\frac{R\Delta\overline{C}_p}{\Delta\overline{S}_i}+\frac{RT}{\Delta\overline{H}_i}\left(\frac{\partial\Delta\overline{H}_i}{\partial N_i}\right)\frac{dN_i}{dT}+\Delta\overline{S}_i-2R\right]}{R^2T^3}, \qquad (15)$$

since $\Delta\bar{H}_i = f(T, N_i)$. . As before $\Delta\bar{C}_p = (\bar{C}_p)_i^l - (C_p)_i^s$ and $\Delta\bar{S}_i = \frac{\Delta\bar{H}_i}{T}$. In order to make use of Equation (15) to determine the form of liquidus curves, we must pass from $\frac{d^2a_i}{dT^2}$ to $\frac{d^2N_i}{dT^2}$. This can be done on the basis of the relation

$$a_i = \gamma_i N_i = f(T, N_i), \tag{16}$$

in which γ_i is the activity coefficient; we then have

$$da_i = \left[\frac{\partial(\gamma_i N_i)}{\partial T}\right]_{N_i} dT + \left[\frac{\partial(\gamma_i N_i)}{\partial N_i}\right]_T dN_i; \tag{17}$$

and

$$\frac{d^2a_i}{dT^2} = 2\left(\frac{\partial\gamma_i}{\partial T}\right)_{N_i}\frac{dN_i}{dT} + 2\left(\frac{\partial\gamma_i}{\partial N_i}\right)_T \cdot \left(\frac{dN_i}{dT}\right)^2 + N_i\left(\frac{\partial^2\gamma}{\partial T^2}\right)_{N_i} + \\ + N_i\left(\frac{\partial^2\gamma_i}{\partial N_i^2}\right)_T \cdot \left(\frac{dN_i}{dT}\right)^2 + \left[N_i\left(\frac{\partial\gamma_i}{\partial N_i}\right)_T + \gamma_i\right]\frac{d^2N_i}{dT^2}. \tag{18}$$

Substituting from Equation (8) in (15) we obtain (denoting the right-hand side of (15) by B):

$$\frac{d^2N_i}{dT^2} = \frac{B}{N_i\left(\frac{\partial\gamma_i}{\partial N_i}\right)_T + \gamma_i} - \\ - \frac{2\left(\frac{\partial\gamma_i}{\partial T}\right)_{N_i}\frac{dN_i}{dT} + 2\left(\frac{\partial\gamma_i}{\partial N_i}\right)_T\left(\frac{dN_i}{dT}\right)^2}{N_i\left(\frac{\partial\gamma_i}{\partial N_i}\right)_T + \gamma_i} - \frac{N_i\left(\frac{\partial^2\gamma_i}{\partial T^2}\right)_{N_i} + N_i\left(\frac{\partial^2\gamma_i}{\partial N_i^2}\right)_T\left(\frac{dN_i}{dT}\right)^2}{N_i\left(\frac{\partial\gamma_i}{\partial N_i}\right)_T + \gamma^i}. \tag{19}$$

In order that Equation (19) may be of practical use, it is necessary to determine the signs and the orders of magnitude of the component terms.

a) Determination of the Signs of Terms in Equation (19).

1) Evidently $B \gtrless 0$

2) The form of the function $\gamma_i = f(T, N_i)$ is unknown, as also are the forms of the functions $\gamma_i = f(T)$ at N_i = constant and $\gamma_i = f(N_i)$ at T = constant, if we know only the constants of the pure components and their fusion diagram. However, the forms of the curves $\gamma_i = f(T)$ and $\gamma_i = f(N_i)_T$ are in general known at sufficiently high N_i. If we plot γ_i as ordinate and N_i or T as abscissa, then in the case of positive departures from Raoult's law we shall obtain curves that fall with rise in N_i or T, are concave to the axis of abscissae, and are asymptotic to the line $\gamma_i = 1$ as $N_i \to 1$ (or $T \to \infty$). In the case of negative departures from Raoult's law we shall obtain curves that are symmetrical toward the line $\gamma_i = 1$. It is important for us that, as a rule, the curves $\gamma_i = f(T)_{N_i}$ and $\gamma_i = f(N_i)_T$ have the same form in the temperature range for heterogeneous equilibrium, which occurs in the given system in the composition range $N_i = 0.8$–1.0. Hence, when $\gamma_i > 1$ $\left(\frac{\partial\gamma_i}{\partial T}\right)_{N_i} < 0, \left(\frac{\partial\gamma_i}{\partial N_i}\right)_T < 0, \left(\frac{\partial^2\gamma_i}{\partial T^2}\right)_{N_i} > 0, \left(\frac{\partial^2\gamma_i}{\partial N_i^2}\right)_T > 0$. When $\gamma_i < 1$ these derivatives have the opposite signs.

3) It is always true that $\frac{dN_i}{dT} > 0$.

4) When $\gamma_i < 1$, the denominator of Equation (19) is positive. We shall prove that it cannot be negative also when $\gamma_i > 1$. In proof of this let us replace $\frac{d\ln a_i}{dT}$ in Equation (14) by $\frac{dN_i}{dT}$, with the aid of Equation (17). We obtain

$$\frac{dN_i}{dT} = \frac{\frac{\Delta\bar{H}_i}{RT^2} - N_i\left(\frac{\partial\gamma_i}{\partial T}\right)_{N_i}}{N_i\left(\frac{\partial\gamma_i}{\partial N_i}\right)_T + \gamma_i}; \tag{20}$$

and as the numerator of the fraction is positive when $\gamma_i > 1$, so also is the denominator (see Paragraph 3).

b) Estimation of the Orders of Magnitude of the Terms in Equation (19). In order to estimate the orders of magnitude of terms of Equation (19) we made the following assumptions: $N_i = 0.9$; $a_i = N_i$; $\Delta\bar{H}_i = \Delta H_i$; $\left(\Delta\bar{S}_i = \Delta S_i;\ \Delta\bar{C}_p = \Delta\bar{C}_p^{*};\ \frac{dN_i}{dT} = \frac{\Delta H_i}{RT^2}\,N_i.\right)$ In order not to underestimate the effect of the term containing $\left(\frac{\partial \Delta\bar{N}_i}{\partial N_i}\right)_T$ on the order of B, we assumed for it the very high value of $\left(\frac{\partial \Delta\bar{H}_i}{\partial N_i}\right)_T = 500$.

1) Estimation of the order of B by the appropriate calculations for Zn, Bi, H_2, H_2O, $FeCl_2$, and C_6H_6 showed that B lies in the range $10^{-4} \geq B \geq 10^{-7}$. Data required for the calculation were taken from the reference books [6] and [8].

2) It was found that for the same substances the values of $\frac{dN_i}{dT}$ lie in the range $10^{-2} - 10^{-3}$.

3) In the estimation of the values of $\left(\frac{\partial \gamma_i}{\partial N_i}\right)_T$ and $\left(\frac{\partial^2 \gamma_i}{\partial N_i^2}\right)_T$ we used Van Laar's Equation [9]:

$$\log \gamma_i = \frac{\alpha_i (1 - N_i)^2}{[1 + (\beta_i - 1) N_i]^2}, \tag{21}$$

in which α_i and β_i are constants (at T = constant) for the i-th component in the given binary mixture. Values of the derivatives were determined for each component of the following mixtures: Hg – Sn, Hg – Cd (323°), H_2O – $CH_3COC_2H_5$ (42.5°), $C_6H_5NH_2$ – C_6H_{12} (25°). The data for α and β were taken from Hildebrand [10] and Dauphin [11]. It was found that the derivatives lie in the ranges $10^{-2} \leq \left(\frac{\partial \gamma_i}{\partial N_i}\right)_T \leq 5 \cdot 10^{-1}$ and $10^{-1} \leq \left(\frac{\partial^2 \gamma_i}{\partial N_i^2}\right)_T$ 5, and in all eight cases the second derivative is of the order of ten times the first.

4) This estimation, made above for substances differing very greatly from one another, presupposes the generalization of our results on orders of magnitude to any real binary system; hence, for the estimation of the orders of magnitude of $2\left(\frac{\partial \gamma_i}{\partial N_i}\right)_T \left(\frac{dN_i}{dT}\right)^2$ and $N_i\left(\frac{\partial^2 \gamma_i}{\partial N_i^2}\right)_T \cdot \left(\frac{dN_i}{dT}\right)^2$, we assumed that $\left(\frac{\partial \gamma_i}{\partial N_i}\right)_T$ is of the order of 10^{-1}, $\left(\frac{\partial^2 \gamma_i}{\partial N_i^2}\right)_T$ is of the order of $5 \cdot 10^{-1}$, and for $\frac{dN_i}{dT}$ we took the calculated values for the substances enumerated in Paragraph 1. It was found that for all these substances

$$N_i\left(\frac{\partial^2 \gamma_i}{\partial N_i^2}\right)_T \left(\frac{dN_i}{dT}\right)^2 > 2\left(\frac{\partial \gamma_i}{\partial N_i}\right)_T \left(\frac{dN_i}{dT}\right)^2 \text{ and } N_i\left(\frac{\partial^2 \gamma_i}{\partial N_i^2}\right)_T \left(\frac{dN_i}{dT}\right)^2 \geq B$$

in order of magnitude, with the exception of H_2O, for which B is of the order of 100 times as great as $N_i\left(\frac{\partial^2 \gamma_i}{\partial N_i^2}\right)_T \left(\frac{dN_i}{dT}\right)^2$.

5) Since

$$\left(\frac{\partial \gamma_i}{\partial T}\right)_{N_i} = -\frac{(\Delta\bar{H}_i)_S}{RT^2}\,\gamma_i, \tag{22}$$

then, assuming that $(\Delta\bar{H}_i)_S$ is of the order of 10 cal/mole and T = 300°K, we obtain $5 \cdot 10^{-5}$ for the order of magnitude of the derivative. As a rough approximation let us assume that the same relation exists between the orders of magnitude of $\left(\frac{\partial^2 \gamma_i}{\partial T^2}\right)_{N_i}$ and $\left(\frac{\partial \gamma_i}{\partial T}\right)_{N_i}$ as between the partial derivatives with respect to mole fraction (see Paragraph 3); in order of magnitude $\left(\frac{\partial \gamma_i}{\partial T^2}\right)_{N_i}$ will be $5 \cdot 10^{-4} > B$; and in order of magnitude $2\left(\frac{\partial \gamma_i}{\partial T}\right)_{N_i} \frac{dN_i}{dT} \leq 10^{-6}$.

Hence, according to our estimation, the sign of $\frac{d^2 N_i}{dT^2}$ is determined by the last term of Equation (19). This implies that the curve for the liquidus of the i-th component in the range $N_i \approx 1$–0.8 (since the estimation

* Probably ΔC_p – Publisher's note.

TABLE 2

No.	System Component (1) – Component (2)	Conforms	Does not conform	Notes	Literature sources
	I. $\gamma_i < 1$				
1	Bismuth-lead	1		Solid solution in (2)	[16, 17]; [18, 19]
2	Benzene-chloroform	1.2			[10]; [20]
3	Allylphenylthiourea-trichloroacetic acid	1		No liquidus branch for (2)	[29]
4	Allylphenylthiourea-acetic anhydride	1		Ditto	[29]
5	Acetanilide-phenol	1		" "	[28]
6	Boron tribromide – stannic bromide	1.2			[30]
	II. $\gamma_i > 1$				
7	Bismuth-cadmium	2	1		[12]; [18]; [21]
8	Copper-bismuth	1		No liquidus branch for (2)	[22]; [18]
9	Zinc-bismuth	1		Solid solution in (2)	[22]; [18]
10	Bismuth-tin	1		Ditto	[16]; [18]
11	Cadmium-tin	1.2			[23]; [18]; [24]
12	Cadmium-lead	1.2			[23]; [18]; [24]
13	Copper-thallium	1		No liquidus branch for (2)	[22]; [18]
14	Zinc-indium	1		Solid solution in (2)	[25]
15	Benzene-stannic bromide	1.2			[26] [10]; [1]
16	Benzene-carbon disulfide	1		No liquidus branch for (2)	[10]; [1]
17	Benzene-methanol	1		No liquidus branch for (2)	[10]
18	Iodine-carbon disulfide	1		Ditto	[10]
19	Iodine-chloroform	1		" "	[10]
20	Iodine-carbon tetrachloride	1		" "	[10]
21	Phosphorus-carbon disulfide	1		" "	[10]
22	Naphthalene-acetic acid	1		" "	[10]
23	Naphthalene-butanol	1		" "	[10]
24	Naphthalene-cyclohexane	1		" "	[10]
25	Naphthalene-acetone	1		" "	[10]
26	Naphthalene-nitrobenzene	1		" "	[10]
27	Biphenyl-heptane	1		" "	[10]
28	Biphenyl-carbon disulfide	1		" "	[27]
29	Uranium hexafluoride-bromine trifluoride	1.2			
30	p-Dibromobenzene-phenol	1		No liquidus branch for (2)	[28]
31	p-Dibromobenzene-aniline	1		Ditto	[28]
32	Naphthalene-phenol	1		" "	[28]
33	Allylphenylthiourea-toluene	1		" "	[29]
34	Allylphenylthiourea-benzene	1		" "	[29]
35	Allylphenylthiourea-aniline	1		" "	[29]
36	Allylphenylthiourea-p-dibromobenzene	1.2			[29]
37	Allylphenylthiourea-naphthalene	1.2			[29]
38	Stannic iodide-boron tribromide	1		No liquidus branch for (2)	[30]
39	Arsenic tribromide-boron tribromide	1		Ditto	[30]
40	Uranium hexafluoride-bromine	1		" "	[31]

of order of magnitude was made for $N_i = 0.9$) will be convex to the composition axis for positive departures from Raoult's law and convex in the opposite direction for negative departures. This conclusion was checked for 48 liquidus curves in the 40 binary systems listed in Table 2. In most systems it was found possible to use only the liquidus curve of one of the components for comparison of theory with experiment, either because there were considerable fields of solid solutions on the side of the second component, or because we had no data on the liquidus curve; this is indicated in the column headed "Notes". The last column gives the literature sources, the first reference being to data on the departure from ideality in mixtures and the second to the information on the fusion diagram; where there is only one reference, all the information comes from the same source.

As will be seen from Table 2, in 47 cases out of 48 cited there is complete accord between theory and experiment. The only exception is bismuth in the system Bi-Cd. However, an examination of the results of Nikolskaya and Gerasimov [12] on the dependence of γ_{Bi} on T and N_{Bi} shows that this exception actually provides confirmation of the correctness of the part played by the last term in Equation (19) and, in particular, of the order of magnitude of $\left(\frac{\partial^2 \gamma_i}{\partial T^2}\right)_{Ni}$. Actually, γ_{Bi} changes smoothly from 1.002 to 1.001 as the temperature is raised from 400° to 650° for $N_{Bi} = 0.9$; γ_{Cd} changes from 1.036 to 1.018 as the temperature is raised from 400° to 500° for $N_{Cd} = 0.9$. At 400° γ_{Bi} changes from 1.000 to 1.002 as N_{Bi} changes from 1.0 to 0.9; γ_{Cd} changes from 1.000 to 1.036 as N_{Cd} changes from 1.0 to 0.9, although $\frac{\partial^2 \gamma_{Cd}}{\partial N^2_{Cd}}_T < 0$. Comparison of these data with the form of liquidus branches of Bi and Cd in the above-indicated ranges of $N_i = 1-0.8$ confirms the correctness of the estimate of the order of magnitude of $\left(\frac{\partial^2 \gamma_i}{\partial T^2}\right)_{Ni}$ and therefore of the part it plays in the determination of the sign of $\frac{d^2 N_i}{dT^2}$: the third term of Equation (19) for Bi in this system is very small and the form of the liquidus branch is determined by the first two terms, which are of the same sign; hence, $\frac{d^2 N_i}{dT^2} > 0$, i.e., the liquidus curve is convex toward the composition axis, which is actually observed in practice. For Cd γ_{Cd} is greatly temperature-dependent and the sign of $\frac{d^2 N_i}{dT^2}$ is determined by the sign of $\left(\frac{\partial^2 \gamma_{Cd}}{\partial T^2}\right)_{NCd}$, i.e., $\frac{d^2 N_{Cd}}{dT^2} < 0$. As pointed out by Nikolskaya and Gerasimov [12], with whom we are in agreement, the Bi-Cd system is an exception with respect to the dependence of γ_i on concentration: in spite of the strong chemical interaction in the system, in the regions $N_{Cd} > 0.8$ and $N_{Bi} > 0.65$ $\gamma_i > 1$ at all temperatures (400-650°). The exceptional character of the behavior of the system Bi-Cd is confirmed also by the fact that in the systems Bi-Pb ($\gamma_i < 1$) and Bi-Sn ($\gamma_i > 1$) the form of the liquidus branch of bismuth corresponds to that predicted on the basis of the estimation of the orders of magnitude of the terms of Equation (19).

TABLE 3

Mixture	$N_1 \approx 0.9$		$N_1 \approx 0.1$		Temperature (°C)
	$\left(\frac{\partial \gamma_1}{\partial N_1}\right)_T$	$\left(\frac{\partial^2 \gamma_1}{\partial N_1^2}\right)_T$	$\left(\frac{\partial \gamma_1}{\partial N_1}\right)_T$	$\left(\frac{\partial^2 \gamma_1}{\partial N_1^2}\right)_T$	
(1) Sn — Hg (2)	—0.0146	+0.18	—7.35	+78.6	323
(1) Hg — Sn (2)	—0.32	+1.18	—0.21	— 0.24	323
(1) H_2O—$CH_3COC_2H_5$ (2)	—0.523	+4.806	—1.78	— 1.017	42.5

It does not appear to be possible to give an exact characterization of the conditions determining the appearance of points of inflection on liquidus curves on the basis of Equation (19), because we do not know the forms of the functions $\Delta\bar{H}_i = f(N_i)_T$, $\gamma_i = f(T)_{Ni}$, $\gamma_i = f(N_i)_T$ and others entering Equation (19); as yet these relationships can be found only experimentally for given concrete systems. It is clear, however, that in principle such a condition is found in the change in the order of magnitude of terms of Equation (19) with change in T and N_i. It is, for example, sufficient for the second term to become greater in absolute magnitude than the third for the sign of $\frac{d^2 N_i}{dT^2}$ to be reversed. Table 3 gives values of $\left(\frac{\partial \gamma_i}{\partial N_i}\right)_T$ and $\left(\frac{\partial^2 \gamma_i}{\partial N_i^2}\right)_N$ for $N_i = 0.9$ and 0.1 for three substances; the calculation was by Equation (21) from data in [10, 11].

As will be seen from Table 3, for Hg and H_2O $\left(\frac{\partial \gamma_1}{\partial N_1}\right)_T$ passes through a maximum and $\left(\frac{\partial^2 \gamma_1}{\partial N_1^2}\right)_T$ passes through zero as N_1 changes from 0.9 to 0.1. At the value of N_1 corresponding to $\left(\frac{\partial^2 \gamma_1}{\partial N_1^2}\right)_T = 0$, a point of inflection may appear on the liquidus curve. In the case of Sn the second derivative increases with concentration more rapidly than the first, so that there should not be a point of inflection here. Unfortunately, the fusion diagrams of these systems do not belong to the eutectic type, which makes it impossible to compare these conclusions with the experimental facts.

The possibility of a linear course of liquidus curves in real systems follows from the possibility of mutual compensation among terms of the right-hand side of Equation (19).

Equation (19) is quite strict and general; it is applicable to any eutectic system, and for ideal systems it passes into Equation (10) or (9). As regards inferences made from the estimation of the orders of magnitude of terms of Equation (19), then, owing to the nature of the assumptions made, they should be applicable to those real systems in which the departures from ideality are not too small. In the future we hope to give quantitative expression to this condition. In the meantime let us point out that, for example, in the systems $C_6H_6 - C_6H_5CH_3$ and $C_6H_6 - C_{10}H_8$ the experimental solubility, according to Kravchenko [13], in the range $N_i = 1.0$-0.8 is less than the ideal value by 0.2-0.4 mole %, i.e., there are small positive departures from ideality. This results in low orders of magnitude for the second and third terms of Equation (19), and the sign of $\frac{d^2N_i}{dT^2}$ is determined by the first term; the liquidus curves are therefore convex toward the composition axis, B being positive for these substances. Hence, if it is desired to decide the type of departure from ideality on the basis of the experimental fusion diagram, the possibility of the existence of such departures must first be determined. Usually, this is not difficult to do on the basis of very general considerations relating to the structures of the molecules of the components.

Hence, in real systems in which the departures from ideality are not too small, the form of the liquidus curves of the components is determined by the character of the temperature- and concentration-dependence of the activity coefficients. As, however, the estimation does not take account of the possibility of exceptions, the conclusions drawn from this estimation may not be applicable in all cases. When we take account of such exceptions as the system Bi-Cd, we may estimate that the conclusions are probably applicable to about 95% of the cases, on the average.

Two conclusions can be drawn from inferences based on the estimate of the parts played by the terms of Equation (19) in determining the sign of $\frac{d^2N_i}{dT^2}$.

1. In systems showing separation into layers in the liquid phase and having only an upper critical point, the liquidus curve on which the layer-separation region lies will be convex toward the composition axis in the range from $N_i = 1$ to the point where separation begins. When there is also a lower critical point, exceptions are possible, and these are the more probable, the higher the layer-separation region lies above the liquidus curve. In both cases exceptions for the liquidus curve of the second component are probable.

2. In systems in which compounds are formed, the liquidus curves of the components should be convex in the direction away from the composition axis. The correctness of this conclusion is confirmed by an examination of experimental data in reference books and monographs (see, e.g., [14, 15]).

SUMMARY

1. The form of liquidus curves in binary systems of the eutectic type having nondissociating components was investigated by methods of mathematical analysis.

2. It was shown that in ideal systems for which $\Delta C_p \equiv 0$ the form of the liquidus curves is determined completely by the entropy change in the passage of the component from the crystalline state to the solution.

3. For $\Delta C_p \neq 0$, the form of the liquidus curves of ideal systems depends substantially on the value and sign of the ratio $\frac{\Delta C_p}{\Delta S_i}$.

4. It was shown that linearity of the liquidus curve is not a criterion of nonideality of the system.

5. In real systems the form of the liquidus curve depends greatly on the type of departure from ideality and the character of the relation of activity coefficient to temperature and concentration.

6. When the departures of mixtures from Raoult's law are not too small, the form of liquidus curves at $N_i = 1.0-0.8$ is associated unequivocally with the type of departure from Raoult's law, so that for $\gamma_i > 1$ the liquidus curves are convex toward the composition axis and for $\gamma_i < 1$ they are convex in the direction away from the composition axis. The proportion of exceptions to this rule should not be more than about 5%.

7. The conclusions concerning the form of liquidus curves of eutectic systems were extended to binary systems with layer separation in the liquid phase ($\gamma_i > 1$) and with compound formation ($\gamma_i < 1$).

8. All the theoretical conclusions were checked against experimental data and were found to be in good agreement with them.

LITERATURE CITED

[1] H. W. Bakhius, Roozeboom, Die heterogenen Gleichgewichte vom Standpunkte der Phasenlehre, 2 Heft, 1 Teil, S. 276. Braunschweig, 1904.

[2] N. V. Lipin, Bull. Inst. Phys.-chem. Anal., 4, No. 1, 48 (1928).

[3] W. Argersinger, Trans. Kansas Acad. Sci. 50, 216 (1947); Cited in C. A. 42, 442f (1948).

[4] V. Mathot, Bul. Soc. chim. Belges 59, 137 (1950).

[5] V. Ya. Anosov, Bull. Sector Phys.-chem. Anal 22, 67 (1953).

[6] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, Selected Values of Chemical Thermodynamic Properties, Washington, 1952.

[7] A. Eucken and E. Schröder, Z. phys. Chem. B 41, 307 (1938).

[8] E. V. Britske, A. F. Kapustinsky, B. K. Veselovsky, L. M. Shamovsky, L. G. Chentsova and V. I. Anvaer, Thermal Constants of Inorganic Substances, Izd. AN SSSR, Moscow, 1949.*

[9] J. J. Van Laar, Z. phys. Chem. 72, 723 (1910); 83, 599 (1913).

[10] J. H. Hildebrand, Solubility of Nonelectrolytes, GONTI, Moscow, 1938.**

[11] J. Dauphin, Bull. 1954, 53.

[12] A. V. Nikolskaya and Ya. I. Gerasimov, J. Phys. Chem. 28, 713 (1954).

[13] V. M. Kravchenko, J. Phys. Chem. 13, 139 (1939).

[14] Landolt-Börnstein, Phys. Chem. Tabellen, 5 Aufl., I (1923).

[15] V. Ya. Anosov and S. A. Pogodin, Fundamental Principles of Physicochemical Analysis, Izd. AN SSSR, Moscow, 1947.*

[16] J. Chipman, Disc. Faraday Soc. 4, 23 (1948).

[17] V. N. Eremenko, O. M. Eremenko and T. P. Bruevich, Ukrain. Chem. J., 17, 658 (1951).

[18] M. Hansen, Structures of Binary Alloys, Metallurgy Press, Moscow, 1941.*

[19] W. E. Barlow, Z. anorg. allg. Chem. 70, 183 (1911).

[20] A. F. Kapustinsky and S. I. Drakin, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1947, 435.

[21] C. T. Heycock, and F. H. Neville, J. Chem. Soc. 61, 895 (1892).

[22] O. J. Kleppa, J. Am. Chem. Soc. 74, 6047, 6051 (1952).

[23] N. W. Taylor, J. Am. Chem. Soc. 45, 2865 (1923).

[24] A. Stoffel, Z. anorg. allg. Chem. 53, 137 (1907).

[25] W. J. Svirbely and S. M. Selis, J. Am. Chem. Soc. 75, 1532 (1953).

[26] A. F. Kapustinsky and Yu. M. Kess.er, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1956, 899.***

[27] J. Fischer and R. C. Vogel, J. Am. Chem. Soc. 76, 4829 (1954).

[28] V. P. Shishokin and M. I. Muskina, Bull. Acad. Sci., Chem. Series No. 4, 793 (1938).

[29] V. P. Shishokin, Bull. Inst. Phys.-chem. Anal., 4, No. 1, 195 (1928).

[30] R. F. Adamsky and C. M. Wheeler, J. Phys. Chem. 58, 225 (1954).

[31] J. Fischer and R. C. Vogel, J. Am. Chem. Soc. 76, 4862 (1954).

N. S. Kurnakov Institute of General and Inorganic Chemistry of the Academy of Sciences of the USSR

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PRINCIPLES UNDERLYING NEW HIGHLY PRODUCTIVE METHODS OF "COMPLEX" CHEMICAL TREATMENT OF POLYMETALLIC IRON ORES*

D. P. Bogatsky and G. G. Urazov**

In previous investigations [1-5] we developed the theoretical basis of methods, new in principle, for the solution of highly important problems relating to the chemical refinement and "complex" treatment of polymetallic iron ores. In particular, as a result of our investigation of the chlorination of garnierite [6], it was shown that preliminary reduction of garnierite results in an appreciable increase in the extent to which it undergoes chlorination. As attempts to chlorinate unreduced silicate-oxide ore [2] gave a much lower extraction of metals than that obtained in the chlorination of garnierite, it appeared desirable to apply "complex" direct reduction as a method of increasing productivity and the degree of chlorination of the valuable components of this ore; this led to the development of new highly productive methods for the chemical refinement and treatment of silicate iron-nickel ores in accordance with the general scheme: reduction – oxidation – reduction. For our investigations we took an untreated, unrefined recalcitrant silicate ore from the waste dump of Alderbak mine, Khalilov region, which is of great interest for industry. In spite of prevailing, firmly held views [7], it was proved for the first time, both theoretically and experimentally, that it is possible to effect efficient "complex" direct reduction of waste silicate ores, and optimum conditions were determined for carrying out this process in a simple fashion in practice [8].

However, in order to develop a method for one refinement of this ore under industrial conditions – and such a method is absolutely essential for increasing the productivity of the plants in operation – it was proposed to subject the ore first to "complex" direct reduction under the conditions that we have found [8] and then to a "chlorinating roast" to convert the metals to be extracted into readily soluble chlorides. These processes, which have not been studied at all, were in need of detailed investigation.

There is an absence of reliable and accurate methods for the experimental study of the physical chemistry and potential productivity of the proposed processes of "complex" direct reduction and subsequent chlorinating roast; this applies also to the hydrometallurgical treatment of chlorinated ore and to the optimum conditions for such treatment from the point of view of maximum extraction of all valuable metals from the ore. First, therefore, we worked on the development of analytical methods for following the course of the complicated processes of leaching out direct-reduction products [9] and of the chlorinating roast, as applied to polymetallic silicate iron ores.

As a result of our study of the physical chemistry, potential productivity, and optimum conditions of processes of leaching out chlorides of iron-group metals from reduced, chlorinated ore with the aid of aqueous solutions of hydrochloric acid of various concentrations and also water under various conditions, we showed that the use of hydrochloric acid for leaching the chloride ash is not essential, since it shows no important advantages over aqueous leaching. The extent to which the most valuable metal, nickel, is brought into solution in the aqueous leaching of the chloride ash bears a roughly linear relation to the temperature of leaching. The iron content of the solutions obtained by aqueous leaching bears some form of inverse relationship to the leaching temperature. Almost the whole of the nickel chloride in the chloride ash is brought into solution by aqueous leaching at the

* The authors use the term "complex" to imply simultaneous utilization or isolation of all useful components. – Publisher.

** Deceased.

boil for only one hour, whereas the iron content of solutions obtained under conditions of almost complete extraction of nickel chloride is only about one-quarter or one-fifth of the nickel content, which corresponds to extraction of iron to the extent of only 0.6-0.7%. Under these conditions leaching of the chloride ash proceeds at an adequate rate and mechanical stirring is quite unnecessary.

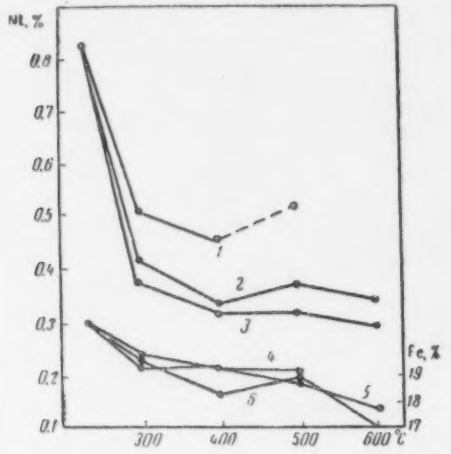

Fig. 1. Lowering of nickel (Curves 1-3) and iron (Curves 4-6) contents in the chlorinating roast as a function of temperature of roasting.

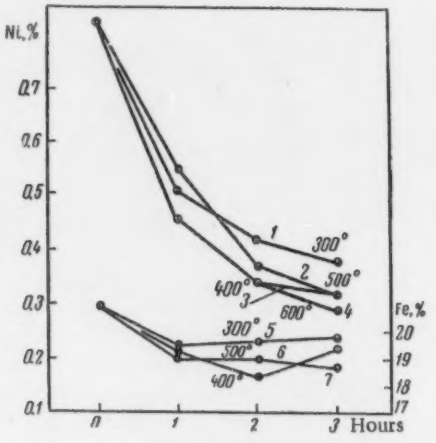

Fig. 2. Lowering of nickel (Curves 1-4) and iron (Curves 5-7) contents in the chlorinating roast as a function of duration of roasting.

The results of our experimental and theoretical study of processes of "complex" direct reduction of the ore under investigation and its chlorinating roasting at 300-600° with subsequent aqueous leaching under the optimum conditions found are shown graphically in Figs 1-3.

Curves 1-3, Fig. 1, and Curves 1-4, Fig. 2, show the lowering of the content of nickel in the silicate-oxide form in the ash from waste ore in its dependence on the temperature and duration of the chlorinating roast. The dependence of the change of iron content on the same factors is represented by Curves 4-6, Fig. 1, and Curves 5-7, Fig. 2. Curves 1-3, Fig. 3, represent the degree of extraction of nickel and Curves 4-6 the degree of extraction of iron as functions of the same factors. It follows from the experimental data given in Fig. 1 that even low-temperature chlorination of reduced recalcitrant waste ore under the most unfavorable conditions of roasting and without any stirring ensures extraction of nickel to the extent of 80.5%. It was shown that there is an approximately linear relationship between the extraction of metals and the temperature or duration of the chlorinating roast. At 600°, not only is ferric chloride volatile, but nickel chloride begins to volatilize appreciably, a process which is quite inappreciable at 550°. In order to avoid loss of nickel chloride by evaporation, the temperature of the chlorinating roast should not be above 550-560°. The highest extraction of nickel without appreciable volatilization of its chloride is obtained under very simple conditions of aqueous leaching of the previously reduced ore treated with chlorine at 500° for three hours without any stirring. As regards the extraction of iron into the solution in the leaching of the ash, it may be regarded as firmly established that the amount passing into solution is extremely slight, varying according to the conditions of the chlorinating roast from traces to 3.8% of its total content in the ore. This is of great practical importance, for in the subsequent precipitation of nickel concentrate or metallic nickel from the resulting solutions the preliminary purification of these solutions from iron is either unnecessary or is considerably facilitated, which greatly simplifies the technical procedure.

These very small amounts of iron, passing into solution in the aqueous leaching of the ash, do not interfere with the formation of a rich nickel oxide concentrate without preliminary purification of the solutions from iron. Thus, experiments on the precipitation of nickel oxide concentrates from the unpurified solutions with milk of lime gave precipitates of hydroxides which, after being dried at 105-110°, gave finished nickel oxide concentrates having nickel contents of 32.51-37.19% and iron contents of 7.14-8.23%. Thus, the nickel content of the nickel oxide concentrates obtained was 50-60 times as high as that of the treated recalcitrant waste ore, and the iron content was only half of that of the ore. No difficulties are foreseen in the practical application of the method

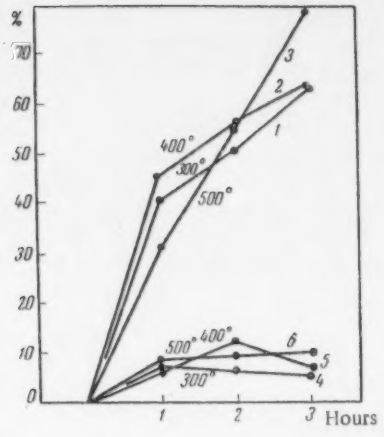

Fig. 3. Extraction of nickel (Curves 1-3) and iron (Curves 4-6) in the aqueous leaching of chloride ash in its dependence on the temperature and duration of the chlorinating roasting of recalcitrant waste ore.

that we have developed, i.e., chlorinating roasting of the ore after its preliminary "complex" direct reduction, for this process is very much simpler than the highly complicated technological procedure for the extraction of nickel and cobalt from the usual silicate-oxide iron-nickel ores, as realized in our present works.

Summarizing and generalizing the results of our investigations of the proposed method of refining low-grade and waste silicate-oxide iron-nickel ores by "complex" direct reduction and subsequent chlorinating roasting, we may regard the following as established: the physicochemical conditions in the proposed method, which consists in a cycle of reactions of direct "complex" reduction of silicate and oxide compounds of iron and nickel with formation of active metallic nickel or ferronickel and in a subsequent intense chlorination of the freshly reduced metals, ensure adequate efficiency of the process. As well as iron and nickel, oxide compounds of cobalt that are present in the ore are also reduced to the metallic state. Hence, the preliminary "complex" direct reduction of the ore has a favorable influence also on the extent of the subsequent chlorination of cobalt, which is often present in small amounts in iron-nickel ores.

Thus, it can be regarded as established that "complex" direct reduction of the ore before its chlorination greatly facilitates the chlorination of all the valuable components of the ore. Also, the reactivity, and therefore the chlorinatability, of other, difficultly reducible components of the barren rock in the ore, is appreciably lowered by the intense high-temperature calcination in the preliminary reduction. The reduction in the chlorinatability of the dead rock of the ore in this method is very considerable in view of the possibility of chlorinating the reduced metals at relatively low temperatures – below the temperatures at which the chlorides of the valuable metals are appreciably volatile. Hence, preliminary "complex" reduction of the silicate and oxide compounds of valuable components of the ore which are capable of being extracted ensures their selective chlorination owing to the considerable lowering of the chlorinatability of unreduced highly calcined components of the dead rock in the ore.

The great readiness with which chlorine reacts with freshly reduced active metals and their solid solutions makes it possible under practical conditions to carry out the chlorinating roast efficiently on reduced ore even at relatively low temperatures, the optimum temperatures under the conditions investigated being in the range 400-500°. According to our investigations, the duration of the chlorinating roast, even in absence of mechanical agitation, need not exceed three hours at the optimum roasting temperature. The negligible or only slight iron content in the nickel-containing solutions obtained by leaching the chloride ash makes it possible to precipitate a rich nickel concentrate from them without any preliminary purification, which considerably simplifies the previously developed scheme of obtaining nickel concentrates from various nickel-containing solutions. The insignificant passage of iron into solution in the leaching of ore treated by the method proposed considerably simplifies also the practical preparation of nickel- containing solutions for electrolysis when electrolytic nickel is to be obtained from them.

In the treatment of oxide and silicate- oxide nickel ores that are at present teated by pyrometallurgical reduction, i.e., are richer than the waste ore investigated, the simple method of aqueous leaching of the product of reductive and chlorinating roasts that we have developed will doubtless have still higher technical and economic advantages. Further radical increase in the productivity of these processes of reductive and chlorinating roasts is, as has been experimentally proved, effected by bringing them together in space and time, which leads us to a new method of high-temperature reductive-oxidative chlorination that has been investigated in detail.

An object of the investigations was to determine the relation of the productivity of the proposed

reductive-oxidative chlorination process to the main technological conditions of treatment. We studied also processes of formation, sublimation, and condensation of the chlorides of the valuable metals to be extracted and the way in which their behavior in the process of reductive-oxidative chlorination depends on the following main technological factors: 1) the temperature of the process; 2) its duration; 3) the degree of grinding of the ore; 4) the consumption of reducing agent; and 5) the effect of activators and other factors that lower the temperature at which the process occurs. In addition, experiments were carried out to determine whether it is possible in principle to bring about selective condensation of the chlorides driven off and to obtain oxide concentrates from these by various methods. In the experimental study of the process of reductive-oxidative chlorination of ore from the point of view of its productivity in relation to apparatus, the conditions required were found to be identical with those for the chlorination of nickelous oxide and garnierite [6-7]. For experiments on the condensation of chlorides on a large laboratory scale we used specially designed apparatus.

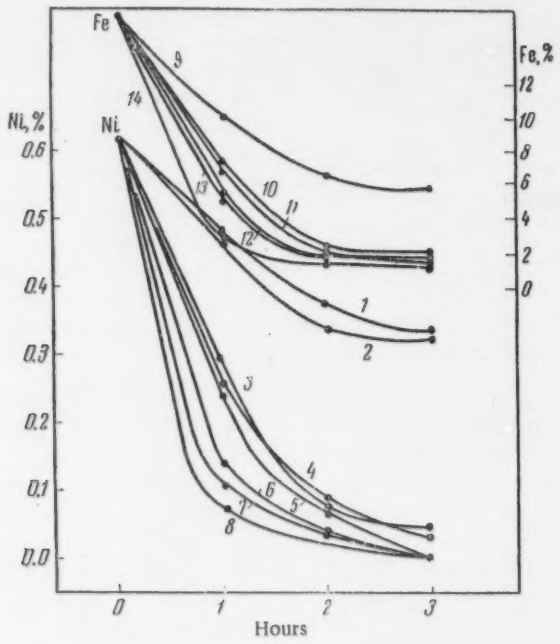

Fig. 4. Relation of the lowering of iron and nickel contents in the process of chlorinating recalcitrant waste ore to the temperature and duration of the process: 1) 700°, 10 mesh; 2) 700°, 35 mesh; 3) 800°, 35 mesh; 4) 800°, 10 mesh; 5) 800°, 6 mesh; 6) 900°, 6 mesh; 7) 900°, 10 mesh; 8) 900°, 35 mesh; 9) 700°, 10 mesh; 10) 800°, 6 mesh; 11) 800°, 10 mesh; 12) 800°, 35 mesh; 13) 900°, 10 mesh; 14) 900°, 35 mesh.

The main results of our investigations are shown graphically in Figs. 4-9. The lowering of the nickel content of the waste ore during its treatment by the proposed method is represented by the lower curves, and the lowering of the iron content by the upper curves (Fig. 4), and in the figures relating to chlorination the degree of chlorination of nickel during treatment of the waste ore is represented by curves in the upper half of the figure, whereas the variation in the chlorination of iron in the same ore is represented by curves in the lower half of the figure.

The experimental results obtained on the reductive-oxidative chlorination of the recalcitrant waste silicate ore from the Khalilov deposits indicate the considerably higher efficiency of this process, as compared with the chlorinating roast of the same ore at 400-500°. As the results show, treatment of this ore by the proposed

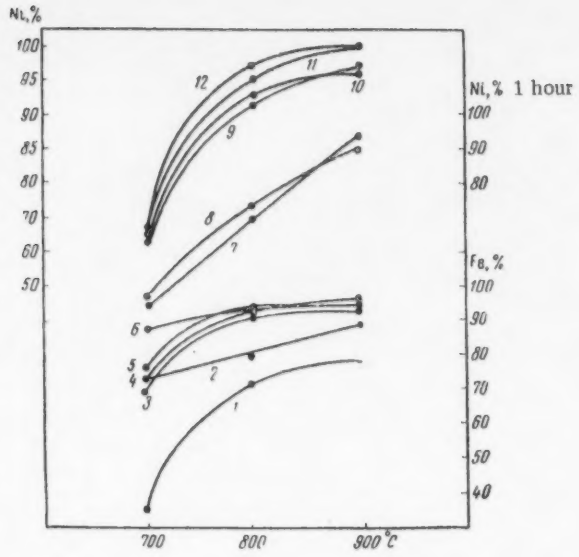

Fig. 5. Relation of the degree of chlorination of recalcitrant waste iron and nickel ore of 10 and 35 mesh to the temperature of the process: 1) 1 hour, 35 mesh; 2) 1 hour, 10 mesh; 3) 2 hour, 35 mesh; 4) 2 hour, 10 mesh; 5) 3 hour, 10 mesh; 6) 3 hour, 35 mesh; 7) 1 hour, 35 mesh; 8) 1 hour, 10 mesh; 9) 2 hour, 10 mesh; 10) 2 hour, 35 mesh; 11) 3 hour, 35 mesh; 12) 3 hour, 10 mesh.

method ensures that, without any difficulty, almost the whole of the nickel is converted into chloride, which volatilizes completely from the ore during the chlorination treatment. Under the conditions for almost complete extraction of nickel the degree of chlorination of iron is also fairly high and attains 90-96%. Special experiments on the large laboratory scale showed that almost complete extraction of cobalt is achieved at the same time. Under the appropriate conditions, high extraction of valuable metals is attained irrespective of the degree of grinding of the ore over the wide range investigated (100-6 mesh).

Under the conditions studied, irrespective of the degree of grinding of the ore, the proposed process is extremely efficient and productive, which ensures its rapid adoption in practice in the effort to attain maximum production indices in the extracting of valuable metals even from recalcitrant waste silicate ores. The effect of various conditions on the efficiency of the process was investigated with the object of lowering the temperature of reductive-oxidative chlorination as much as possible, and it was shown that, without change in the extent of extraction of valuable metals and without increase in the duration of the process, the temperature can be lowered to 700° and the consumption of low-grade coal dust to 5% of the weight of ore treated. In this respect, the productivity of the chlorination process was affected favorably by the use of carbon tetrachloride and of a pyrites-charcoal filter as activators of the process and also by the introduction of sulfides, in particular pyrites, into the charge undergoing chlorination. The use of carbon tetrachloride as activator is a practical possibility owing to its fairly simple preparation from technical and natural gases containing methane and other hydrocarbons. Under the proposed conditions, in which the processes of "complex" direct reduction of the ore and its chlorination are combined in one apparatus, the formation of this activator can occur directly in the combined process of reduction and chlorination, which will increase its activating effect still more.

In addition to the activating effect of carbon tetrachloride vapor, the effect of the presence of sulfur chloride vapor in the gaseous chlorine on the course of chlorinating processes was investigated. In spite of the fact that sulfur chloride is obtained as a by-product in the manufacture of carbon tetrachloride, i.e., both these activators are obtained simultaneously with corresponding reduction in their cost, we used also simpler

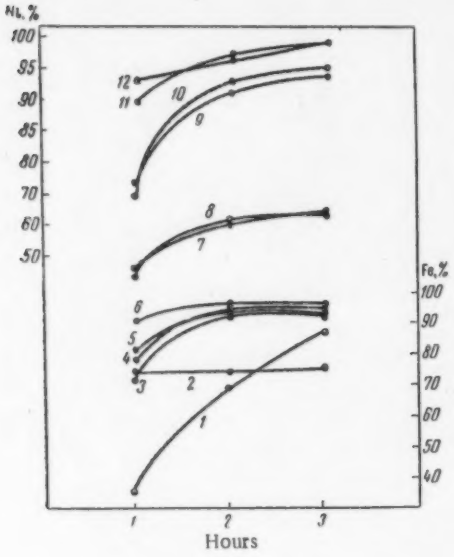

Fig. 6. Relation of the degree of chlorination of the iron and nickel of recalcitrant waste ore of 10 and 35 mesh to the duration of the process: 1) 700°, 35 mesh; 2) 700°, 10 mesh; 3) 800°, 35 mesh; 4) 900°, 35 mesh; 5) 800°, 10 mesh; 6) 900°, 10 mesh; 7) 700°, 10 mesh; 8) 700°, 35 mesh; 9) 800°, 10 mesh; 10) 800°, 35 mesh; 11) 900°, 10 mesh; 12) 900°, 35 mesh.

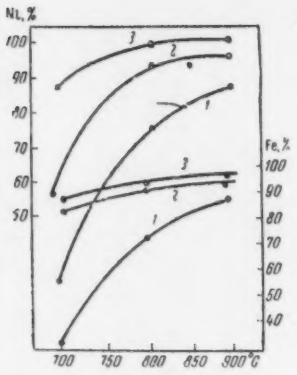

Fig. 7. Relation of the degree of chlorination of the iron and nickel of recalcitrant waste ore of 6 mesh to the temperature of the process: 1) 1 hour; 2) 2 hours; 3) 3 hours.

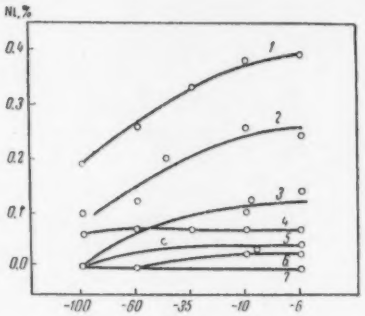

Fig. 9. Extent of extraction of nickel in the chlorination of recalcitrant waste ore as a function of degree of grinding: 1) 700°, 3 hours; 2) 800°, 1 hour; 3) 900°, 1 hour; 4) 800°, 2 hours; 5) 800°, 3 hours; 6) 900°, 2 hours; 7) 900°, 3 hours. (The ordinates represent content of unextracted nickel in the treated recalcitrant waste ore).

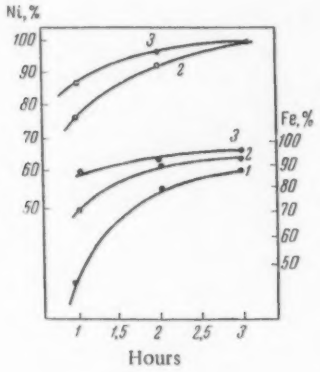

Fig. 8. Relation of the degree of chlorination of the iron and nickel of recalcitrant waste ore of 6 mesh to the duration of the process: 1) 700°; 2) 800°; 3) 900°.

methods of formation in the course of the process. As sulfur chloride is formed by the action of gaseous chlorine on metal sulfide, the introduction of this activator into the chlorine was carried out by passing the latter through a pyrites-charcoal filter heated in a tube furnace at various temperatures. Experiments were carried out also on the direct formation of sulfur chloride in the sphere of reaction in the chlorination process, this being achieved by addition of pyrites to the ore being chlorinated. This is of great importance from the industrial point of view if cobalt-containing pyritic tailings from concentrating plants are utilized as sulfur-containing additions. In this case the process of preparing the activator is combined with extraction of cobalt from pyritic tailings, with substantial increase in the efficiency and economy of the process. Although almost complete chlorination of valuable metals is attained at 700°, nickel chloride is not always driven off completely at this temperature; the optimum temperature for the process must therefore be considered to be 800°.

Our experiments showed not only the practical possibility of the complete volatilization of nickel, cobalt and iron chlorides from the treated ore, but also the absence of any difficulty in principle in the process of condensing them. This gives us grounds for the view that no substantial difficulties will be met in practice from the point of view of the apparatus for this process. As our investigations showed, carrying out the process of fractional selective condensation of the sublimed chlorides is somewhat more complicated. Our investigations already make it possible for us to effect the fractional condensation of nickel and nickel-cobalt chloride condensates, which may then be converted into oxide concentrates. The oxide concentrates were prepared by hydro- and pryo-metallurgical methods. The hydrometallurgical preparation of nickel-cobalt oxide concentrates consisted in simple precipitation of the corresponding hydroxides from solutions of the chlorides, for which purpose sodium hydroxide solution and milk of lime were used. The use of sodium hydroxide is sound practice in view of its formation as a by-product in the manufacture of chlorine, which must be carried out at the works in which nickel and cobalt are manufactured, whether they be made by the method considered here or by methods already in use. However, the use of milk of lime for precipitation of the hydroxides has also great possibilities from the point of view of economy.

The pyrometallurgical preparation of nickel-cobalt oxide concentrates from the condensates of chlorides was carried out by an original method.

In order to achieve the greatest simplicity and economy we proposed and investigated a process of oxidative roasting of nickel-cobalt chloride condensates in air. It was found that complete oxidation was attained in 5-6 hours at 500° and in 3-4 hours at 550°.

Our experiments on the hydro- and pryo-metallurgical preparation of nickel-cobalt oxide concentrates from chloride condensates showed that it is possible to carry out these processes in a very simple fashion in practice. Nickel-cobalt chloride condensates obtained by the chlorination of the waste ore under investigation contained 5.85-8.35% of nickel, 0.44-0.78% of cobalt, 12.63-18.93% of iron, 1.97-3.52% of chromium, and 0.35-0.58% of manganese, and these yielded nickel-cobalt oxide concentrates containing 12.02-34.85% of nickel, 0.70-4.82% of cobalt, and 2.73-32.12% of iron. In view of the completely inadequate amount of study devoted to this matter, the nickel-cobalt oxide concentrates obtained cannot in any way be regarded as optimum from the point of view of nickel and cobalt contents. These contents can be substantially raised by driving off iron chloride, which we have shown experimentally to be a practical possibility. Iron chloride can be removed almost completely from the nickel-cobalt condensate by roasting it in an atmosphere of chlorine for 3-5 hours at 350-400°. As a result of the sublimation of iron chloride from nickel-cobalt chloride condensates their nickel content was raised from 5.35% to 7.14-8.15% and their cobalt content from 0.44% to 0.77%. These tentative qualitative data indicate the possibility in principle and the adequate simplicity in operation of the proposed processes of chlorine-refining of nickel-cobalt condensates.

The investigations that we have now carried out show that the method that we have developed for chlorine reductive-oxidative treatment of low-grade and waste silicate-oxide iron-nickel-cobalt ores by "complex" direct reduction and chlorination combined in space and time is an extremely efficient and productive "complex" process ensuring almost complete extraction of iron, nickel, cobalt, and other valuable metals from these ores. The degree of chlorination of iron, nickel and cobalt under the optimum conditions for the proposed processes attains 100%. Almost complete extraction of iron, nickel and cobalt is attained already at temperatures ranging from 700° to 850-900°, even from recalcitrant waste silicate ore. The optimum duration of the process of reductive-oxidative chlorination of silicate ore at these temperatures is three hours. Under these conditions it is also quite easy to attain almost complete sublimation of iron, nickel and cobalt chlorides from the ore. The complete possibility of "complex" and fractional condensation of the sublimed chlorides was proved experimentally. Collective and selective concentrates were prepared from recalcitrant unrefined silicate ore. In the collective nickel-cobalt chloride concentrates the degree of concentration of nickel attained 9.3 and that of cobalt 17.6. A selective nickel chloride concentrate containing 31.21% of nickel was obtained, the degree of concentration of nickel being 49.5. Detailed study of the behavior of iron and nickel in the chlorination of the investigated recalcitrant waste silicate iron-nickel ore by the proposed method showed that the degree of chlorination of iron and nickel bears an approximately linear relationship to temperature and duration of process within the ranges investigated. Almost complete extraction of nickel in the chlorination of the recalcitrant waste ore was attained at temperatures of 700°, 800°, and 900°.

The time required in the chlorination process for almost complete extraction of nickel from this ore bears

some sort of an inverse relationship to the temperature of the process. The time required varies from one to three hours, depending on the other conditions obtained in the chlorination process. The temperature and duration of the chlorination process necessary for almost complete extraction of nickel from the ore bear inverse relationships to the consumption of carbonaceous reductant under the conditions investigated. The amount of the very lowest grade of anthracite dust required varies from 5% to 7% on the weight of the recalcitrant waste ore, depending on the other conditions of the chlorination process. Irrespective of the extent to which the ore is ground, almost complete extraction of nickel is effected in the chlorination process. No well defined relationship was established between the extraction of nickel and the degree of grinding of the ore under the conditions investigated. The temperature and duration of the chlorination process necessary for almost complete extraction of nickel bear a rather vague inverse relationship to the degree of grinding of the ore within the investigated limits.

Our study of the effect of various activators on the productivity of the chlorination process points the way to further simplification and increased efficiency with lowering of the temperature and shortening of the duration of this process. In particular, in this connection we see the possibility and desirability of simultaneous efficient treatment of cobalt-containing pyritic tailings and other sulfide materials by the proposed process. Technological conditions have been established for the complete sublimation of iron, nickel, and cobalt, after which ore chlorinated under the conditions investigated is completely spent, so that the scheme of treatment that we have devised is exceptionally simple.

The possibility of obtaining nickel-cobalt oxide concentrates by the method proposed was checked and proved experimentally; almost complete extraction of nickel and cobalt was attained in the precipitation of solutions of the respective concentrates.

Hence, the extraction of valuable metals as an oxide concentrate is always determined in practice by the high degree of their chlorination and therefore only by their very full extraction from the ore in the process of reductive-oxidative chlorination.

The nickel content of the nickel oxide concentrates obtained was brought to 34.85% with an iron content of 2.73-8.23%. A degree of concentration of nickel of 55 was attained in these oxide concentrates. The cobalt content of the nickel-cobalt concentrates was brought to 4.82% and can be increased further; the degree of concentration of cobalt attained 188-192. The main conditions for carrying out the proposed process of pyrometallurgical preparation of nickel-cobalt concentrates were tentatively established. Oxidative roasting of nickel-cobalt chloride concentrates at 500° for 5-6 hours gave nickel-cobalt oxide concentrates. The nickel content of nickel-cobalt oxide concentrates obtained from recalcitrant waste ore by the pyrometallurgical method was brought to 12.0-13.15%, and it can be raised further in the ways that we have envisaged. The degree of concentration of nickel attained in nickel-cobalt oxide concentrates obtained by the pyrometallurgical methods varied from 19 to 21.

A method that is technically more rational than chemical-metallurgical refining is the electrolytic isolation of the valuable metals from solutions of their chlorides [10, 11] with regeneration of chlorine. This results in the "complex" preparation of high-quality pure metals from low-grade and waste silicate-oxide iron-nickel-cobalt ores by the methods proposed.

As a result of our investigations, the substantial technical and economic advantages of the methods that we have developed for the "complex" chemical treatment and refining of polymetallic iron ores can be considered to be proved experimentally. These advantages are: 1) more complete extraction of valuable metals from the ore and higher speed of processing, as compared with the methods now used in the Ural works; 2) the essentially "complex" character of the process proposed and the possibility of extracting metals other than iron, nickel and cobalt; 3) the simpler and more compact schemes of extracting valuable metals, as compared with those now used; 4) applicability to waste and silicate-oxide iron-nickel-cobalt ores which cannot be utilized at the present owing to the absence of an effective method for refining and treating them; 5) the extreme compactness of the process under manufacturing conditions from the point of view of apparatus, it being possible to obtain concentrates, metals, and alloys in a single continuously operating aggregate; 6) absence of the higher toxicity and explosion hazards associated with the carbonyl methods of obtaining the same metals—methods borrowed from foreign technology and now established in our industry.

SUMMARY

1. As a result of theoretical and experimental investigations on various reductive-oxidative and other processes carried out with the object of developing new methods of solving the problem of the "complex" utilization of ores of iron-group metals, very simple and effective methods are proposed for their chemical refinement and treatment based on the theoretical scheme of reduction-oxidation-reduction.

2. It was proved experimentally that application of the principle of selective activation of the metals to be extracted with simultaneous chemical deactivation of the components of the dead rock considerably increases the productivity and the technical and economic effectiveness of the processes of "complex" chemical treatment of polymetallic ores of iron-group metals.

3. The new methods developed for the chemical refinement and treatment of polymetallic ores make possible effective "complex" utilization not only of normal, but also of recalcitrant waste silicate ores which are not utilized at present owing to the absence of industrial methods for their refinement and treatment.

4. The technical and economic advantages of the methods developed are discussed.

LITERATURE CITED

[1] D. P. Bogatsky, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1944, 272.

[2] D. P. Bogatsky, Bull. Acad. Sci. USSR, Div. Chem. Sci. 6, 891 (1946); 12, 1809 (1946).

[3] D. P. Bogatsky, Bull. Acad. Sci. USSR, Div. Chem. Sci. 10, 1512 (1949).

[4] D. P. Bogatsky and G. G. Urazov, Bull. Acad. Sci. USSR, Div. Tech. Sci. 9, 108 (1955).*

[5] G. G. Urazov and D. P. Bogatsky, Bull. Acad. Sci. USSR, Div. Chem. Sci. 10 (1956).*

[6] D. P. Bogatsky, Proc. Acad. Sci. USSR 45, 2, 65 (1944).

[7] D. P. Bogatsky, Collection of Sci. Papers of Moscow Inst. of Nonferrous Metals and Gold 3, 6, 58 (1938).**

[8] D. P. Bogatsky, Bull. Acad. Sci. USSR, Div. Chem. Sci. 12, 1809 (1946).

[9] G. G. Urazov and D. P. Bogatsky, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1956, 1029.

[10] G. G. Urazov, Metallurgy of Nickel. ONTI 1935.**

[11] I. N. Plaksin and D. M. Yukhtanov, Hydrometallurgy, Metallurgy, Press, 1947.**

N. S. Kurnakov Institute of General and Inorganic Chemistry of the Academy of Sciences of the USSR

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EFFECT OF THE MOLECULAR STRUCTURE OF AN ALCOHOL ON THE KINETICS OF ITS DEHYDROGENATION

COMMUNICATION 3. COMPARISON OF RESULTS FOR VARIOUS ALCOHOLS

A. A. Balandin, O. K. Bogdanova, and A. P. Shcheglova

In previous communications [1, 2] we gave the results of an investigation on the kinetics of the dehydrogenation of ethyl, propyl, allyl, isopropyl, butyl, isopentyl, and phenethyl alcohols over an oxide catalyst. A general summary of the results is given in Tables 6 and 7 in [2]. It was found that the reaction differs from the already known action of metallic copper on an oxide catalyst, which also acts selectively and brings about dehydrogenation, in that both the reaction rate and also other kinetic characteristics are appreciably dependent on the structure of the alcohol molecule. We now examine the question of the laws determining the effect of the structure of the alcohol molecule on the kinetics of its dehydrogenation.

Effect of Structure on the Rate Constant of the Reaction

The extent to which the structure of the alcohol molecule affects the rate at which it is dehydrogenated can be judged by a comparison of the data given in the previous communications [1, 2]. Thus, the temperatures at which a given yield (30%) of aldehyde (or ketone) is obtained differ by 64° for isopropyl and propyl alcohols, by 10° for propyl and butyl alcohols, and by 58° for propyl and allyl alcohols. Under given conditions at 342°, isopropyl alcohol reacts to the extent of 55.0% whereas allyl alcohol reacts to the extent of only 5.5%. Hence, the oxide catalyst investigated acts selectively on the various alcohol molecules.

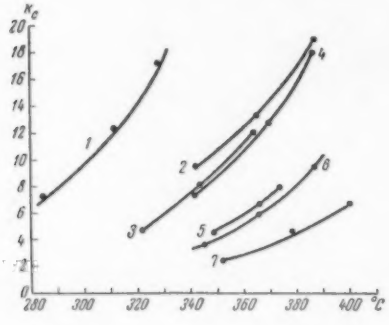
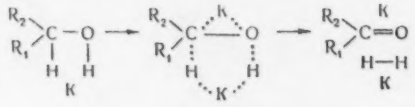


Fig. 1. Effect of temperature on the dehydrogenation rate constant: 1) isopropyl alcohol; 2) isopentyl alcohol; 3) butyl alcohol; 4) propyl alcohol; 5) phenethyl alcohol; 6) ethyl alcohol; 7) allyl alcohol.

In the complex quantity, reaction rate, let us first examine one component, the rate constant. In Fig. 1 the ordinates are dehydrogenation rate constants given in [2] for the seven alcohols investigated, and the abscissae are temperatures. The curves in Fig. 1 show that the various alcohols fall in a definite order and that this order depends on their structures. It will be seen that the dehydrogenation rate constants rise in the following order: allyl, ethyl, phenethyl, propyl, butyl, isopentyl, and isopropyl alcohols. The secondary isopropyl alcohol is dehydrogenated much more rapidly than the primary propyl alcohol. As is well known, the rate constant is also a complex quantity and, according to the Arrhenius equation, depends on the activation energy ϵ and the action constant k_0. In the previous investigations [1, 2] we determined ϵ and k_0 for various alcohols; below we make separate examinations of the dependence of ϵ and k_0 on the structures of the alcohols.

Effect of Structure on Activation Energy

According to the multiplet theory [3], in the dehydrogenation reaction alcohol molecules come into contact with the catalyst K through their reacting group of atoms [included in the frame shown in scheme (1)].



(1)

The general expression for the activation energy ϵ given in [4] for the dehydrogenation of primary alcohols [R_2 = H in scheme (1)] becomes

$$\varepsilon \approx 0{,}75\,\{[Q_{CH} + Q_{OH} + a(R_1)] - [Q_{CK} + Q_{OK} + a'(K, R_1)] - \\ - 2Q_{HK} - \lambda(K)]\} \qquad (2)$$

Q are mean energies of bonds between atoms in the molecule or atoms and catalyst K, as indicated in the subscript; $a(R_1)$ is the increment of the bond energies Q_{CR} and Q_{OH} in the molecule arising from the introduction of the substituent R_1 – it is a function of the nature of this substituent; $a'(K,R_1)$ is the analogous increment of energies of bonds of atoms with the catalyst Q_{CK}, Q_{OK}, and Q_{HK}, and this increment is dependent on the natures of both R_1 and K; and $\lambda(K)$ expresses the effect of atoms of the catalyst surrounding the active center on the energy of bonds formed with the catalyst. When, for a given K, one substituent is replaced by another, ϵ changes by $\delta\epsilon$ and, as we have shown and as can be shown also from Equation (2),

$$\delta\varepsilon = 0{,}75\delta a(R_1) - 0{,}75\delta a'(K, R_1). \qquad (3)$$

It is well known that, owing to changes in electron density, substituents affect bond energies. Thus for C–H bond energies in hydrocarbons we have $C_2H_5 - H = 96$; $n\text{-}C_3H_7 - H = 100$; $n\text{-}C_4H_9 - H = 101$ and $i\text{-}C_3H_7 - H = 94$ kcal [5] (here and in the further discussion all energies are expressed in units per mole). On the other hand, as shown previously [6-8], in the dehydrogenation of primary alcohols over copper ϵ remains almost unchanged as the number of carbon atoms changes from 1 to 5 in the unbranched chain R_1. This implies that $\delta\epsilon = 0$ and that the first and second terms of the right-hand side of Equation (3) are mutually compensating.

In secondary alcohols a further substituent R_2 appears in Scheme (1) so that a term in (R_2) must be added in the first expression in brackets in Equation (2) and a term in (K,R_2) must be added in the second. In passing from a primary alcohol to a secondary we have

$$\delta\varepsilon = 0{,}75b(R_2) - 0{,}75b'(K, R_2), \qquad (4)$$

as will be clear from the above. This is in accord with the observation that in passing from primary to secondary alcohols in dehydrogenation over copper we find that a change in ϵ occurs.

When we pass from copper (K) to an oxide catalyst (K_1), the terms in Equation (2) depending on K are changed so that for primary alcohols the change in ϵ for this transition will be

$$\delta\varepsilon = -0{,}75\delta a'(K, R_1) - 0{,}75\delta\lambda(K). \qquad (5)$$

For an oxide catalyst, with change in R_1, Equation (3) with K_1 instead of K should be valid, and therefore

$$\delta\varepsilon = 0.75\delta a(R_1) - 0.75\delta a'(K_1, R_1). \qquad (6)$$

As the present investigation [1, 2] shows, with change of R_1 over an oxide catalyst $\delta\epsilon \neq 0$, i.e., the compensation is disturbed. This is not in conflict with theory, for, comparing Equations (3) and (6), we see that they

differ in the second term of the right-hand side. The cause of the lack of compensation will be considered below.

Consider primary alcohols I and II which differ in the nature of R_1. As already shown [4], as we pass from I to II

$$\delta\varepsilon < 0, \quad \text{if} \quad \delta a < \delta a', \tag{7}$$

i.e., if the condition that $a_{II} - a_I < a'_{II} - a'_I$ holds. Hence, the activation energy will be less for alcohol II than for alcohol I; $\delta\epsilon < 0$ if the differences in the effect of the substituents are less in the original alcohol molecules than in their radicals – residues of the alcohols attached to the catalyst – which form the limiting state of the intermediate complex. In the present work we found ϵ and $\delta\epsilon$ experimentally for the dehydrogenation of alcohols over an oxide catalyst.

The following regularities were observed: as pointed out above, ϵ depends on the nature of the substituents; moreover, the position (α or β) in which the substituents occur is of significance. Let us take ethyl alcohol as our starting point; it has ϵ = 17.7 kcal (Table 7 in [2]). Replacement of an α-hydrogen by a methyl group lowers ϵ to 12.8 kcal, so that $\delta\epsilon$ = 4.9 kcal. This is in accord with Equation (4). Replacement of β-hydrogen also affects ϵ, and the effect of the nature and structure of the substituent is notable. β-Substitution of phenyl raises ϵ by 0.3 kcal, for phenethyl alcohol has ϵ = 18.0 kcal. On the other hand, β-substitution of methyl lowers ϵ by 2.1 kcal, for propyl alcohol has ϵ = 15.6 kcal. β-Substitution by ethyl lowers ϵ by 1.2 kcal, for butyl alcohol has ϵ = 16.3 kcal. Lengthening and branching of the chain in isopentyl alcohol, for which ϵ = 12.9 kcal, lowers ϵ still further – by 4.8 kcal as compared with ethyl alcohol – and here we have β-substitution by two radicals, methyl and ethyl. Replacement of two β-hydrogens of ethyl alcohol by $=CH_2$ leaves ϵ almost unchanged (for allyl alcohol ϵ = 17.5 kcal). It is possible that the formation of a double bond raises ϵ (being analogous to the effect of the benzene ring in phenethyl alcohol) and the introduction of a carbon atom, even in the form of a methylene group, lowers ϵ and these two effects are mutually compensating.

It follows from this discussion that lengthening of the hydrocarbon chain in a primary alcohol lowers ϵ for the reaction under consideration. Actually, for C_2H_5OH ϵ = 17.7; for C_3H_7OH ϵ = 15.6; for C_4H_4OH ϵ = 16.3; for $C_5H_{11}OH$ ϵ = 12.9 kcal. Butyl alcohol, for which the lowering of ϵ is less than for propyl alcohol, is somewhat out of place. We observed a similar discrepancy in ϵ in another investigation [9], in which we attempted to explain this fact on the partial formation of butadiene.

The effect of α- and β-substitution on the activation energy for the dehydrogenation of alcohols over an oxide catalyst finds an analogy in the similar effect in the dehydration of alcohols [8, 10].

However, the changes in ϵ in the process under investigation have rather the character of corrections: the activation energies for the dehydrogenation of the various alcohols are fairly constant, the variation being from 18.0 to 12.7 kcal at the most, and generally very much less. Hence, the previous conclusion that in dehydrogenation alcohols are oriented with the reacting group toward the catalyst [3, 6] still holds, being confirmed by new experimental material.

Effect of Structure on the Action Constant k_0

The constant k_0 varies symbatically with ϵ (Fig. 2, in which log k_0 is plotted on the same graph as ϵ, but on a different scale). As in previously known cases [11-13], k_0 is related logarithmically to ϵ (Fig. 3). In Fig. 3 the data for five alcohols fit well to the straight line $\epsilon = \underline{a} \log k_0 + \underline{b}$, in which $\underline{a} = 3.2 \cdot 10^3$ and $\underline{b}$ = 4500 kcal; for two alcohols (isopentyl and allyl) there are small discrepancies, probably associated with structural factors. In its physical meaning, the constant $\underline{a}$ is the reciprocal of the so-called scattering factor of active centers [12, 14]. In this case, unlike others observed previously, $\underline{b} \neq 0$, which is clearly not in conflict with theory [12, 14].

The observance of a logarithmic relation – or the θ rule, as it is sometimes called – is of special interest in the present case, for experiments with all the alcohols were carried out over the same sample of catalyst, the activity of which was shown to be constant. The catalyst surface was therefore always the same. Moreover, rate constants, not yields based on amount of substance passed, were measured. Hence, the existence of a logarithmic relationship has been fairly strictly confirmed experimentally.

We see that in dehydrogenation of alcohols the kinetic characteristics vary in a regular fashion. We shall now consider data on adsorption at active dehydrogenation centers.

Effect of Structure on Free Energy and Displacement Equilibrium

The relative adsorption coefficients of oxygen-containing dehydrogenation products z_2 (i.e., the ratios between the adsorption coefficients of the aldehyde (or ketone) and the corresponding alcohol) are equilibrium constants for the adsorptional displacement of alcohols A_1 by the corresponding aldehydes (or ketones) A_2 from the catalytically active surface S [15].

$$A_1S(\ ^s\ ) + A_2(g\ ) = A_2(\ s\ ) + A_1(g\ ). \tag{8}$$

This treatment of the values of z_2 is confirmed by experiments with labeled atoms [16]. As we pass along an homologous series, z_2 increases (see Table 7 in [2]). Thus, for CH_3CHO $z_2 = 2.3$; for C_2H_5CHO $z_2 = 3.4$; for n-C_3H_7CHO $z_2 = 3.5$; for i-C_4H_9CHO $z_2 = 5.7$. It will be obvious that ΔF changes in the same order – see Equation (2) in [1] and Table 7 in [2]. In this respect an oxide catalyst differs from metallic copper, for which z_2 remains constant in an homologous series [7, 8] and $\Delta F = 0$ [17].

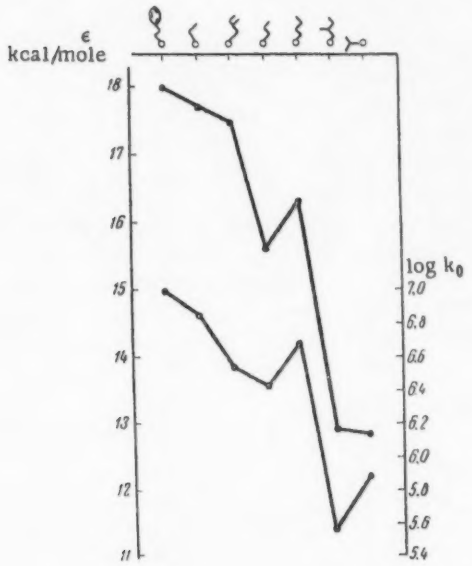


Fig. 2. Activation energy ε and logarithm of the action constant log k_0 for the dehydrogenation of various alcohols.

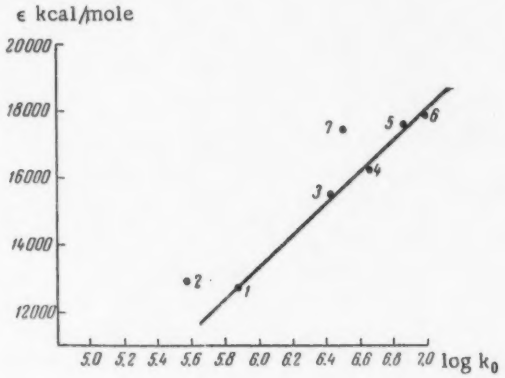


Fig. 3. Logarithmic relation between ε and k_0 for the dehydrogenation of various alcohols over an oxide catalyst (the numbering of the alcohols is the same as in Fig. 1).

Effect of Structure on the Heat of Adsorptional Displacement – ΔH

The change in enthalpy ΔH in adsorptional displacement from active dehydrogenation centers also varies for alcohols of different structure, see Table 7 in [1] and Table 5 in [2]. Comparing ΔH for different alcohols, we note that oxygen atoms, and also carbon-carbon double bonds, are adsorptionally the most active. In fact, if we again take ethyl alcohol as our standard, as we diminish the oxygen content of the alcohol the heat of displacement – ΔH at first diminishes. Thus, for C_2H_5OH – ΔH = 22.1; for C_3H_7OH – ΔH = 11.2; for i-C_3H_7OH – ΔH = 11.0; for C_4H_9OH – ΔH = 11.4, but for $C_5H_{11}OH$ – ΔH increases; – ΔH = 17.5 kcal. It is probable that here, in isopentyl alcohol, we see the effect of double substitution on a β-carbon atom. The introduction of a double bond – transition from propyl (– ΔH = 11.2) to allyl alcohol (–ΔH = 16.4) – and also introduction of a benzene ring – transition from ethyl alcohol to phenethyl alcohol (–ΔH = 27.5 kcal) – raise the heat of adsorptional displacement.

Effect of Structure on Change of Entropy in Adsorptional Displacement

At a given temperature, e.g., 345°, the variation of ΔS is parallel to that of ΔH, as will be seen from Fig. 4. Even in the case of isopentyl alcohol, which did not conform to the preceding regularity, the parallelism between ΔH and ΔS is preserved. It should be noted that the existence of a parallelism between ΔH and ΔS was observed previously for some chemical reactions that were similar among themselves [18]. We have here observed, for the first time, a similar regularity for adsorption processes occurring at catalytically active centers.

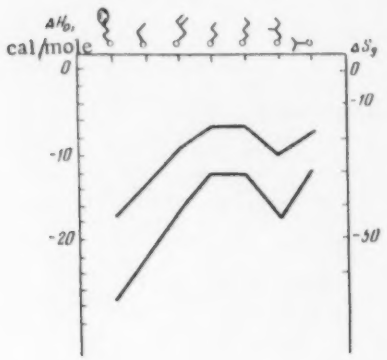


Fig. 4. Parallelism between ΔH and ΔS for the process of adsorptional displacement at catalytically active centers.

It is natural to ask whether the relation is between ε and ΔH or between log k_0 and ΔS. The results of the present work indicate that in some cases there is an antibatic relation between these quantities, though this is not always true. As will be seen by comparison of Figs. 2 and 4, an antibatic relation between ΔH and ε (and also between ΔS and log k_0) is observed for phenethyl, ethyl, allyl, propyl, and possibly butyl alcohols, but not for isopentyl and isopropyl alcohols. A further accumulation of data will allow us to solve this question.

Part Played by Hydrogen Bonding in Dehydrogenation over Oxides

The results of the present investigation prompt the following important question: what is the explanation of the fact that both the dehydrogenation rate constant and the adsorption coefficients (and therefore also the component terms in these coefficients) are constant for various alcohols and aldehydes over copper, but vary according to chemical structure over an oxide catalyst? We find the answer in the formation of an intermediate compound in which the alcohol is attached to the oxide through a hydrogen bond. Such a compound is not a catalytically active form, but its formation has a great effect on the catalysis. In the formation of alcohols and aldehydes on copper, such a compound is not formed because metals do not from stable hydrogen bonds. In the adsorption of the alcohol ROH on the oxide, a hydrogen bond is formed with the oxygen of the oxide ROH...OM. In the adsorption of an aldehyde or ketone not containing a hydroxy group on the oxide, no hydrogen bond is formed.

Under the influence of the new factor – formation of an intermediate compound containing a hydrogen bond – the profile of the potential surface of the reaction is changed; in dehydrogenation over oxides compensation no longer occurs in the expression (6) and the kinetic characteristics of the dehydrogenation of alcohols change with change of structure. Owing to the formation of a hydrogen bond in the adsorption of the alcohol, there is also a disruption of the similarity between this adsorption complex and that of the aldehyde, such as is observed on copper. In the adsorptional displacement equilibrium constant (relative adsorption coefficient), the corresponding factors no longer cancel out, as they do in the case of copper [19]. Hence, over oxides, with change in structure the adsorption characteristics also change.

It should be noted that the calculation of adsorption entropy can be approached also from the point of view of models and the sums of the states derived from them [20], as was done for the dehydrogenation of alcohols over copper [19]. This is an interesting problem for further theoretical consideration.

Our experimental investigation shows that the selective action of the catalyst on reaction rate is an overall effect made up of the selective actions of the catalyst on ε and k_0 for the reaction and on ΔH and ΔS for adsorption. As theory shows, in their turn these values also are complex (see Equation (2) and others).

SUMMARY

1. It was shown that the structures of alcohol molecules affect the activation energy and Arrhenius action constant for the dehydrogenation reaction in a regular fashion; this applies also to changes in enthalpy and entropy of adsorptional displacement on an oxide catalyst.

2. The existence of a logarithnic relation between activation energy and action constant was confirmed.

3. It was shown that there is a parallelism between changes in enthalpy and entropy in the adsorptional displacement of alcohol molecules by the corresponding aldehydes or ketones from active dehydrogenation centers.

4. The part played by hydrogen bonding in dehydrogenation over oxides was discussed.

LITERATURE CITED

[1] O. K. Bogdanova, A. A. Balandin, and A. P. Shcheglova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 787 (1957). *

[2] Idem, Ibid., 795 (1957).*

[3] A. A. Balandin, Questions of Chemical Kinetics and Reactivity, Moscow, 1955, p. 441.**

[4] A. A. Balandin, Proc. Acad. Sci. USSR 97, 667 (1954).

[5] T. L. Cottrell, The Strengths of Chemical Bonds, L., 1954.

[6] W. G. Palmer, F. H. Constable, Proc. Roy. Soc. A, 107, 255 (1925).

[7] A. A. Balandin, J. Phys. Chem. 14, 1160 (1940).

[8] A. Kh. Bork, J. Phys. Chem. 14, 1289 (1940).

[9] A. A. Balandin and A. A. Tolstopyatova, Proc. Acad. Sci. USSR 94, 49 (1954).

[10] H. Dohse, Z. phys. Chem. (B), Bodenstein Festb., 533 (1931).

[11] A. A. Balandin, J. Phys. Chem. 4, 251 (1933).

[12] G. M. Schwab, Catalysis from the Point of View of Chemical Kinetics, (Translation from German), Leningrad, 1934, p. 174.

[13] S. Z. Roginsky, Adsorption and Catalysis at Heterogeneous surfaces, Moscow and Leningrad, 1948.**

[14] A. A. Balandin, Proc. Acad. Sci. USSR 93, 55, 272, 475 (1953)

[15] A. A. Balandin, O. K. Bogdanova, and A. P. Shcheglova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 4, 723 (1955).*

[16] A. A. Balandin, M. B. Neiman, O. K. Bogdanova, G. V. Isagulyants, A. P. Shcheglova and E. I. Popov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 157 (1957).*

[17] A. A. Balandin, Proc. Acad. Sci. USSR 63, 33 (1948).

[18] G. S. Parks and H. M. Huffman, Free Energies of Some Organic Compounds (Translation from English), ONTI, 1936.

[19] A. A. Balandin, Proc. Acad. Sci. USSR 63, 535 (1948).

[20] C. Kemball, Catalysis. Questions of Theory and Methods of Investigation (Translation from English), Moscow, 1955, p. 256.

N. D. Zelinsky Institute of Organic Chemistry
of the Academy of Sciences of the USSR

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VARIOUS TYPES OF BONDS IN CHEMISORPTION ON SEMICONDUCTORS

F. F. Volkenshtein

(Paper read at International Congress on Catalysis at Philadelphia, US, September, 1956)

Chemisorption, with which we are usually concerned in catalysis, differs from so-called physical adsorption in the nature of the forces holding the adsorbed molecule on the adsorbent surface. If the adsorption forces are van der Waals forces – electrostatic-polarization or electrical-image forces – we speak of "physical adsorption," but if the forces responsible for adsorption are chemical in nature (exchange forces) we are concerned with so-called "chemisorption."

In the theoretical examination of physical and chemical adsorption, substantially different approaches to the problem are necessary. In physical adsorption the action of the adsorbent on the adsorbate can be regarded as a feeble perturbation and the problem may be solved within the framework of perturbation theory. In chemisorption the adsorbed molecule and the adsorbent lattice form a single quantum-mechanical system and must be regarded as a single unit. In this case adsorption consists in the formation of a chemical compound between the molecule and the crystal.

We consider here the simplest case of chemisorption – adsorption of a univalent electropositive atom A (i.e., an atom having one electron in excess of a closed shell) on an ionic crystal of the type MR (M is a metal and R a nonmetal) built up from the ions M^+ and R^-. The results can be extended to the case of any binary lattice in which there are homopolar bonds in addition to the ionic bonds. Most semiconductors that can act as catalysts (oxides and sulfides) have lattices of this type. Also, all our considerations can be extended in their entirety to the case of a univalent electronegative atom, i.e., an atom having not an excess, but a deficiency of one electron with respect to a closed shell (in this case, however, the words "electron" and "hole" must always be interchanged in the further treatment), and also to the case of any radical having one free valence. Such free atoms or radicals can appear at a surface in the adsorption of a saturated molecule as a result of the dissociation (as often happens) of such a molecule at the moment of adsorption. The next communication• will be devoted to the adsorption of saturated molecules.

The author has shown [1-5] that bonds of three types are possible between the atom A and the MR lattice, and we have called them "weak" homopolar bonds, "strong" homopolar bonds, and ionic bonds. Let us examine each of these types of bonds.

The "Weak" Homopolar Bonds

We shall ignore the electron and "hole" gases always present at some concentration or other in a crystal (this assumption will later be dispensed with) and shall regard the M^+ and R^- ions in the lattice as point charges. With this approximation we are dealing with a one-electron problem. The only electron is the valence electron of the atom A. While the atom A is sufficiently far removed from the crystal surface its valence electron is entirely its own, but when the atom A approaches the surface its electron is no longer entirely its own, but, strictly speaking, belongs to the system as a whole (Fig. 1). Calculation shows that, if the atom A is situated on a positive M^+ ion of the lattice, as shown in Fig. 1b, the valence electron of A is more or less drawn from the atom A into the lattice. In other words, the electron cloud surrounding the positive core of A and having spherical symmetry in the case of an isolated atom is now deformed and is to some extent spread out into the lattice.

• See Translation page 955.

The wave function of our electron is constructed as a linear combination of the wave functions of the atom A and all the M atoms of our lattice. It can be shown that such a wave function has an attenuated character and fades away inside the lattice as the distance increases from the M^+ ion that forms the adsorption center. The extension of the electron cloud into the lattice determines also the bond formed between the adsorbed atom A and the crystal. It can be shown that the greater this extension (which depends on the natures of the atom and of the lattice), the stronger the bond. This extension leads, among other things, to the acquisition of a certain dipole moment by the adsorbed atom A. It should be noted that it can be shown that the value of this dipole moment, which is purely quantum-mechanical in origin, may exceed that of the dipole moment induced in physical adsorption by a factor of several powers of ten.

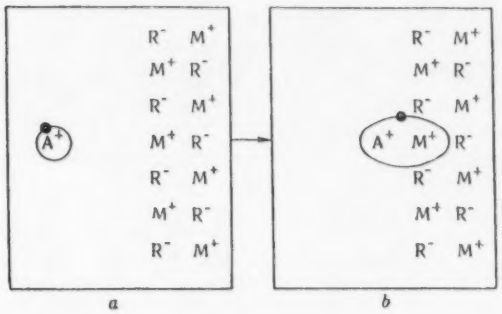

Fig. 1

Hence, the bond between the atom A and the lattice is effected by the valence electron of the atom A. We obtain a bond of the same type as in the molecular ion H_2^+; i.e., a single-electron bond. It should be noted that the valence electron of atom A remains unpaired, i.e., the adsorbed atom A remains with its valence unsaturated.

A bond of this type we shall call a "weak" homopolar bond. The adsorbed atom A, being in a state of "weak" homopolar linkage with the surface, forms a structural defect disturbing the strictly periodic structure of surface. With respect to the free electrons and holes of the crystal lattice, this structural defect plays a double role: in general, it acts both as a localizing center for a free electron and as a localizing center of a free hole.

The localization of an electron or hole on an adsorbed atom A in a state of "weak" homopolar linkage with the crystal results, as we shall see below, to change in the character of the bond between the atom and the crystal. As a result of the localization of an electron a "weak" homopolar bond is converted into a "strong" homopolar bond, and as a result of the localization of a hole it is converted into an ionic bond.

The "Strong" Homopolar Bond

Let us examine the problem of the behavior of a free electron in a lattice on the surface of which there is an adsorbed atom A in a state of "weak" homopolar linkage to the surface. We now have a two-electron problem: the valency electron of the atom A, which brings about the linkage, plus the free lattice electron.

It can be shown that such an adsorbed atom forms a "trap" for a free electron wandering in the conductivity zone. In the energy spectrum of the crystal, such an atom is represented as a local acceptor level, as shown in Fig. 2a, in which $\overline{v}$ is the affinity energy of the adsorbed atom A with respect to the free lattice electron. The transition of the free electron from the conductivity zone to the local level of A means that this electron is localized around the adsorbed atom A. It can be shown that the degree of localization is the greater, the lower the local level (i.e., the greater $\overline{v}$ in Fig. 2a).

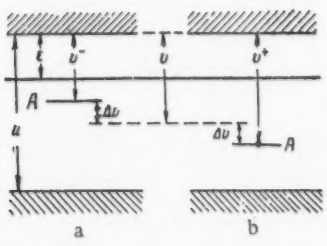

Fig. 2

The position of the level of A (i.e., the distance $\overline{v}$ in Fig. 2a) is determined by the nature of the lattice and the nature of the adsorbed atom. Other conditions being equal, it depends on the distance between the atom A and the crystal surface. As the atom A is removed from the surface, the local acceptor level (Fig. 2a) retracts, as can be shown, into the conductivity zone ($\overline{v}$ diminishes) and the lattice electron situated in this level is gradually delocalized, i.e., its wave function becomes more and more blurred. In the limit, when the atom A is infinitely far removed from the surface, the local level is drawn into the zone and the electron situated in this level is therefore completely delocalized and so has returned to the family of free electrons.

It should be noted that the free lattice electron can be treated as a free positive valence wandering about the crystal. In fact, the presence of electron in the MR lattice indicates that one of the M^+ ions of the lattice has been converted into a neutral M atom. This state of neutrality can move about the lattice, being transmitted from one M^+ ion to the next. The M^+ ion has a closed electron shell, i.e., has an inert-gas structure. The free lattice electron is therefore an extra electron situated on an M^+ ion outside a closed shell and therefore fulfilling the function of a free valence.

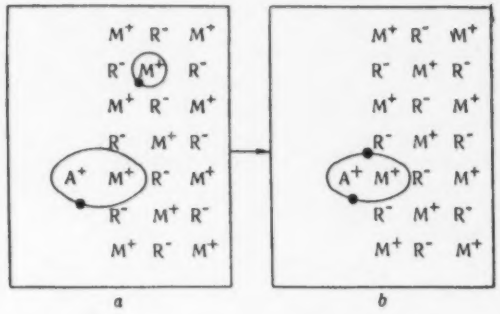

Fig. 3

If the adsorbed atom A, attached to the surface by a "weak" homopolar (i.e., one-electron) bond, captures a free lattice electron, this electron will pair with the valence electron of A and the one-electron bond be converted into a more stable two-electron bond (Fig. 3). The atom A and the lattice electron are then bound together by forces of the exchange type. In this case it is these exchange forces that constitute the adsorption forces holding the atom A on the surface and, in addition, keeping the lattice electron in the vicinity of A. We obtain a bond of the same type as that in the H_2 molecule.

A two-electron bond in which a lattice electron borrowed from the family of free electrons takes part we shall call a "stable" homopolar bond. It should be noted that in the state of "stable" homopolar linkage the valence of the atom A is saturated; it is saturated by the free valence of the surface. In this case the adsorbed atom (in its combination with the adsorption center) is an electrically charged system, as can be seen, for example, from Fig. 3b.

The Ionic Bond

Structural defects having simultaneously both acceptor and donor functions are well known in the theory of the solid state. As an example we have the so-called F-center (an electron at a vacant nonmetal lattice point). As is well known, an F-center may capture a free electron and become so-called F'-center. In this case the F-center plays the part of an acceptor and in relation to the free lattice electron may be represented as a local acceptor level. The F-center may also donate its electron to the conductivity zone or capture a hole from the valence zone. In this case we are concerned with the dissociation of the F-center with decolorization of the crystal. In this the F-center plays the part of a donor and can be represented as a local donor level.

Atom A, adsorbed on the surface of an ionic crystal and present in a state of "weak" homopolar linkage with the surface, forms a structural defect of just this sort. It has affinity for an electron, and at the same time it has affinity for a hole, i.e., it can be represented both as a local acceptor level and as a local donor level, as shown in Fig. 2b. The electron situated in the local level of A in Fig. 2b is not an electron foreign to the atom A, i.e., is not an electron from the crystal lattice, but is one of the atom's own (valence) electrons. Here v^+ is the ionization energy of the adsorbed atom A and $(u - v^+)$ is the energy of the affinity of atom A to a free hole.

It should be noted that the presence of "holes" in the MR crystal generally indicates the presence of a neutral R atom among the R^- ions of the lattice. This local state is, of course, not localized, but can wander about the lattice by transmission from one R^- ion to the next. The hole, therefore, consists in the absence of an electron on one of the R^- ions. In as much as the R^- ion has a closed electron shell and the presence of a hole indicates that one electron has been removed from the closed shell, the hole in the lattice can be treated as a negative free valence. The localization of a hole around the adsorbed atom A present in a state of "weak" homopolar linkage with the lattice results in the breakdown of this linkage and the formation of an ionic bond, as represented in Fig. 4.

In the case of an ionic bond, as also in the case of a "strong" homopolar bond, the valence of atom A is saturated, these cases being different, therefore, from that of the "weak" homopolar bond, in which the valence of atom A remains unsaturated. In the case of the ionic bond, however, the positive valence of atom A is

saturated not by a positive surface valence (as it was in the "strong" homopolar bond), but by a negative surface valence. Under these conditions the adsorbed atom will be positively charged (ionized).

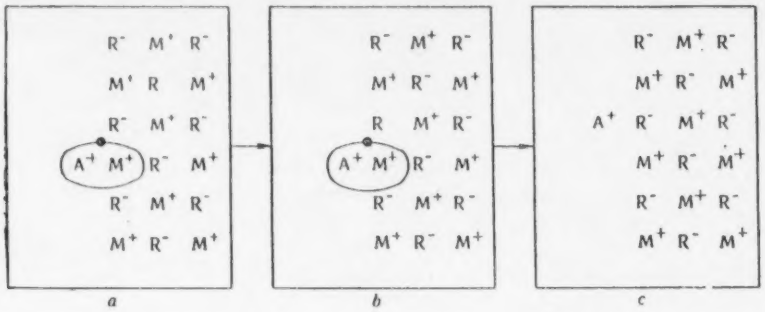

Fig. 4.

The mutual saturation of two valences of the same sign (the positive valence of atom A plus the free positive valence of the surface) results as usual in the formation of a homopolar bon, and the mutual saturation of two valences of opposite sign (the positive valence of atom A plus the free negative valence of the surface) leads to the formation of an ionic bond. Whereas in the transition from the state of "weak" to that of "strong" homopolar linkage the adsorbed atom A acts as an acceptor, in the transition from the state of "weak" homopolar linkage to the state of the ionic bond the same atom acts as a donor.

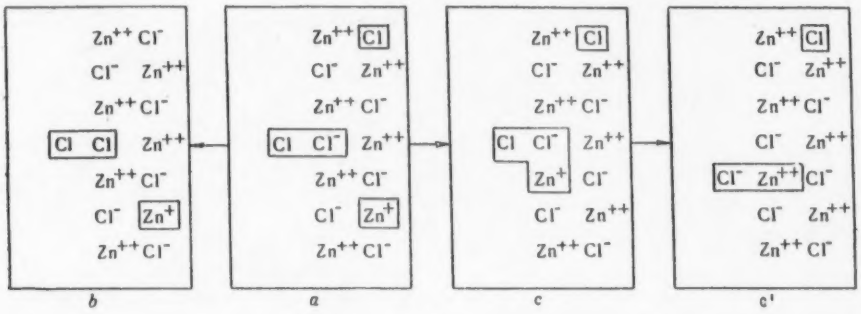

Fig. 5.

Equilibrium Between Various Forms of Chemisorption

In this way we have arrived at the various forms of chemisorption, which differ in the character of the bond between the adsorbed atom and the adsorbent lattice. By way of example let us examine the adsorption of a Cl atom on a $ZnCl_2$ crystal, which can be represented as being built up from Zn^{++} and Cl^- ions. It should be noted that in such a crystal the presence of a free electron indicates the presence of a Zn^+ ion among the Zn^{++} ions of the lattice and the presence of a free hole indicates the presence of a neutral Cl atom among the Cl^- ions. Figure 5 represents the different forms of chemisorption of a Cl atom on a $ZnCl_2$ crystal: "weak" homopolar bond (Fig. 5a), "strong" homopolar bond (Fig. 5b), and ionic bond (Fig. 5c or 5c'). In this case the "strong" homopolar bond is effected by attracting a hole and the ionic bond by attracting an electron.

The different forms of chemisorption can undergo transitions into one another. In other words, the adsorbed atom, while remaining in the adsorbed state, can pass from a state of one type of bonding to a state associated with bonding of a different type, which implies localization or delocalization of a free electron or free hole around the adsorbed atom.

Let us examine the case of established electronic equilibrium. Of the total number of N atoms adsorbed per unit of surface, let N^0 atoms be in the electrically neutral state, let N^- atoms be associated with an electron, and let N^+ atoms be associated with a hole. Clearly,

$$N^0 + N^- + N^+ = N$$

Let

$$\eta^0 = \frac{N^0}{N}, \quad \eta^- = \frac{N^-}{N}, \quad \eta^+ = \frac{N^+}{N}.$$

These quantities characterize the relative contents of the different adsorbed forms or, in other words, the probabilities for the adsorbed atom to be in one or other of the states (characterized by one or other type of bond with the surface).

From the equations of Fermi statistics we obtain the following expressions for these probabilities:

$$\left.\begin{aligned}
\eta^0 &= \frac{1}{1 + 2e^{-\frac{\Delta v}{kT}}\cosh\left(\frac{v-\varepsilon}{kT}\right)} \\
\eta^- &= \frac{e^{\frac{v-\varepsilon}{kT}} - \frac{\Delta v}{kT}}{1 + 2e^{-\frac{\Delta v}{kT}}\cosh\left(\frac{v-\varepsilon}{kT}\right)} \\
\eta^+ &= \frac{e^{\frac{\varepsilon-v}{kT}} - \frac{\Delta v}{kT}}{1 + 2e^{-\frac{\Delta v}{kT}}\cosh\left(\frac{v-\varepsilon}{kT}\right)}
\end{aligned}\right\}$$

in which ϵ is the level of the chemical potential calculated from the bottom of the conductivity zone; the meanings of v and Δv are clear from Fig. 2.

We see that the relative contents of the different forms of adsorption at equilibrium is determined, other things being equal, by the position of the level of chemical potential ϵ. The relation of η^0, η^-, and η^+ to ϵ is shown in Fig. 6. As the level ϵ is displaced downward (from the conductivity zone to the valence zone) η^- falls regularly, η^+ rises regularly, η^0 passes through a maximum.

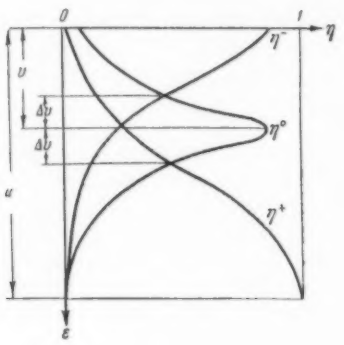

Fig. 6

The position of the level of chemical potential depends on, among other things, the total number N of atoms adsorbed per unit surface. Hence, the relative content of the various adsorbed forms depends on the surface coverage. In other words, the probability that a given atom will be found in a state having a given type of linkage depends on how many atoms are adsorbed on the surface. Hence, each adsorbed atom behaves as if it feels the presence of the remaining atoms, though direct interaction between them is absent (we have ignored it).

The position of the level of chemical potential depends also on the nature and concentration of impurities contained within the crystal. With increase in the content of acceptor impurity the level ϵ moves downward, the donor impurity acts in the opposite direction. Hence, the relative amounts of the different forms of adsorption depends on the nature and amount of the impurities introduced into the crystal.

In this way the properties of the inside are reflected in the properties of the surface.

It should be noted that the so-called "Randschichttheorie der Adsorption" (I have in mind the work of Aigrain and Dugas [6], Weiz [7], Germain [8], and Engel and Hauffe [9]) takes account only of the ionic form of adsorption, the other forms of adsorption being completely ignored. In this way it excludes the possibility of change in the character of the bond formed by the adsorbed atom with the adsorbent surface during the period in which the atom is in the adsorbed state.

Surface Charge. Reactivity of Adsorbed Atoms

The relative contents of the various adsorbed forms determine the extent to which the surface is charged, i.e., the value and sign of the total electric charge concentrated on the surface. This total charge has the value

$$e(\eta^+ - \eta^-)N,$$

in which e is the absolute value of the charge on the electron (according to Randschichttheorie this charge is ± eN). As the level ϵ moves downward in Fig. 6, the algebraic value of this total charge rises in a regular fashion. For $\epsilon < \underline{v}$ the surface is negatively charged; for $\epsilon > \underline{v}$ it is positively charged; and for $\epsilon = \underline{v}$ it remains electrically neutral in spite of the presence of adsorbed atoms on it.

The reactivity of the adsorbed atom naturally varies according to the character of the bond attaching it to the surface. Actually, an atom attached by a "strong" homopolar bond or by an ionic bond is present on the surface in the form of a valence-saturated species (Fig. 7b and 7c); when attached by a "weak" homopolar bond, it forms a free surface radical (Fig. 7a). As a first approximation it may be considered that only the adsorbed atoms that are in this last state will be reactive, and the value of η^0 may be regarded as a criterion of the reactivity of the adsorbed atom.

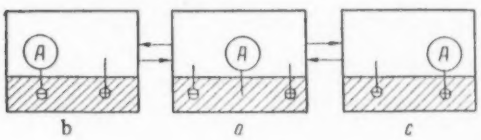

Fig. 7

The factors that displace the level of chemical potential in the crystal will in consequence change the reactivity η of the adsorbed atoms and so change the catalytic activity of the surface. We see that the reactivity η^0 is found to be dependent on the surface coverage and also on the nature and amount of impurity present inside the crystal. In this way we reveal the mechanism of the promoting and poisoning effects of impurities. It should be noted that this mechanism cannot be accomodated within the framework of the Randschichttheorie, according to which all adsorbed atoms are always in the same state and in which the very concept of "reactivity" (in the form in which we introduced it above) loses its meaning.

SUMMARY

The possibility of the formation of various types of bonds between a given atom and a given adsorbent is a characteristic feature of chemisorption. In this respect chemisorption, which is chemical union between a solid and a foreign atom, differs from the usual chemical compounds, which are formed by union between atoms or groups of atoms with formation of molecules. The bond between two atoms (or two groups of atoms) inside a molecule always has a quite definite character, determined unequivocally by the nature of the two components entering into the bond.

The existence of bonds of different types in the chemisorption of the atom A on the ionic crystal MR is determined ultimately by the presence in such a crystal of free electrons and "holes" which fulfill the function of free positive and negative valences respectively and may be drawn (or may not be drawn) into participation in the bond.

LITERATURE CITED

[1] F. F. Volkenshtein, J. Phys. Chem. 21, 1317 (1947).

[2] F. F. Volkenshtein, J. Phys. Chem. 26, 1462 (1952).

[3] F. F. Volkenshtein, J. Phys. Chem. 28, 422 (1954).

[4] F. F. Volkenshtein and S. Z. Roginsky, J. Phys. Chem. 29, 485 (1955).

[5] F. F. Volkenshtein, in the Collection "Problems of Kinetics and Catalysis," Izd. AN SSSR, Moscow, 1955, 8, 79.*

[6] P. Algrain and C. Dugas, Z. Elektrochem. 56, 363 (1952).

[7] P. B. Weiz, J. Chem. phys. 21, 1531 (1953).

[8] J. E. Germain, Compt. rend 238, 236, 245 (1954); J. Chim. phys. 51, 263 (1954).

[9] H. J. Engel and K. Hauffe, Z. Elektrochem. 57, 762 (1953); H. J. Engel, Halbleiterprobleme, No. 1, 249 (1954). K. Hauffe, Ang. Chem. 67, 189 (1955);

Institute of Physical Chemistry of
the Academy of Sciences of the USSR

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* In Russian.

MECHANISM OF THE CATALYTIC ACTION OF SEMICONDUCTORS

F. F. Volkenshtein

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Essential stages in all heterogeneous catalytic reactions are the stages of adsorption and desorption. Gas molecules are first adsorbed on the surface of the solid; they then react, while in the adsorbed state, among themselves or with molecules coming in from the gas phase; and finally the reaction products are desorbed. A catalytic reaction, therefore, is a reaction proceeding at the interface of two phases (solid and gas).

The main task of the theory of catalysis is to provide an answer to the question: why does transfer of a reaction from the gas phase to the surface of a solid result in increased reaction rate ? In order to answer this question we must first elucidate the process that always forms the first stage of any heterogeneous catalytic process – the stage of adsorption.

In the previous communication* we examined the adsorption of univalent atoms and free radicals on the surface of a semiconductor. In the present communication we examine the adsorption of saturated molecules [1-6].

Free Valences on the Surface of a Catalyst

It was shown in the previous communication that free electrons and "holes" of the crystal lattice can take part in the formation of chemical bonds between adsorbed atoms and the adsorbent lattice and in this way perform the function of positive and negative free valences respectively. These free valences play a leading part in the heterogeneous catalytic process; they have the following properties.

1. Each free valence has a certain average life, i.e., a valence can appear and disappear. The crystal is continually producing and absorbing valences. In an ideal crystal the appearance of a positive valence is always accompanied by the formation also of a negative valence. The disappearance of valences also proceeds in pairs and consists in the recombination of an electron and a hole.

2. These valences are not localized in the lattice, but are able to wander over the crystal. This means that a free valence may, with equal probability, be encountered at any point of the crystal.

3. The equilibrium concentration of free valences in a crystal depends not only on the nature of the crystal, but also on the conditions: it increases with rise of temperature and can be artificially increased or diminished as a result of external influences on the crystal, e.g., by irradiation of the crystal by radiation of suitable frequency and by introduction of acceptor or donor impurities. The concentration of free valences depends also on the nature and amount of foreign atoms or molecules adsorbed on the surface, i.e., on "surface impurities;" it can be shown that it changes in the process of adsorption and during reactions between atoms and molecules adsorbed on the surface.

4. We now point out a property of the free valences associated with the crystal surface. In general, free valences in the sense defined above are to be found both on the surface and in the inside of the crystal. In catalytic processes, of course, only the surface valences take part. However, there is a continual exchange of valences between the inside and the surface: valences may leave the surface for the inside, and vice versa.

The inside of the catalyst, therefore, can play the part of a reservoir, absorbing free surface valences and, on the other hand, providing them for the surface. When electronic valence equilibrium is established, movement of valences from the surface is compensated by movement into the surface, so that we have a

* See page 948.

stationary concentration of free valences unequivocally related to the concentration of electron and "hole" gas inside the crystal. Factors affecting the concentration of electron and hole gas inside the crystal affect the concentration of free valences on the surface and so also the catalytic properties of the surface.

The role of free electrons and holes as free valences is manifested not only in the adsorption of free atoms, but also in the adsorption of saturated molecules – in which, in fact, it is manifested most clearly.

Dissociation of Molecules on Adsorption

We shall first investigate the adsorption of a diatomic molecule AB in which each atom has one valence electron. We are therefore concerned with a molecule in which two atoms A and B are united by a single bond. A typical example of such a molecule is H_2. Let us imagine that the molecule AB is approaching the surface of a crystal in the way shown in the upper part of Fig. 1.

We shall treat the matter as a three-electron problem: one valence electron in each of the atoms A and B plus a free lattice electron (an electron in the conductivity zone of the crystal). Calculation shows that with the approach of the molecule AB to the crystal two types of states can arise in the system.

First, there are states in which the free lattice electron (which in the case of an infinitely distant molecule belongs to the conductivity zone of the crystal) continues to remain free. These states are characterized by wave functions with real values of the quasi-impulse; they correspond to energy levels forming a continuous band (conductivity zone). States of this type do not give adsorption.

Second, as well as these states a state may arise in which, as AB approaches the crystal, the free lattice electron becomes more and more localized on the crystal surface around the point to which the molecule AB is approaching (point M in the upper part of Fig. 1). This state is characterized by a wave function with a complex value of the quasi-impulse. This state corresponds to a local energy level, separated from the conductivity zone. Hence, the approach of the molecule AB to the crystal surface results in localization of the free lattice electron. The degree of localization increases as the molecule approaches the crystal. This state results in adsorption. The bond between the molecule and the lattice is formed with the aid of this localized lattice electron.

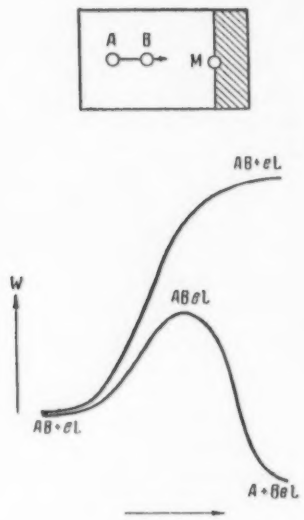

Fig. 1

It can be shown that, as the molecule approaches the crystal, i.e., as the distance between the atom B and the surface diminishes, the distance between the atoms B and A increases. In other words, as the bond between the atom B and the crystal grows stronger, the bond linking A to B so as to form a molecule becomes weaker. This is represented in the lower part of Fig. 1.

In Fig. 1, the reaction coordinate is plotted along the axis of abscissae and the energy of the system W along the vertical axis. The cross-hatched region corresponds to a state of the first type, in which the free lattice electron remains free, i.e., takes no part at all in the game. The lower curve corresponds to a state of the second type. As we move from left to right in Fig. 1, the lower curve moves away from the upper cross-hatched region. In other words, the distance between the local level and the conductivity zone increases. At the same time, the degree of localization of the electron from this level increases.

The left part of Fig. 1 corresponds to the state

$$AB + eL$$

(free AB molecule plus a free electron in the conductivity zone, which we denote by the symbol eL). The right part of the lower curve in Fig. 1 corresponds to the state

$$A + BeL$$

This is a state in which the atom A is free (i.e. the bond between the atoms A and B is broken), but the atom B is attached to the surface by a "strong" homopolar (two-electron) bond in which the valence electron of the atom B and the lattice electron take part.

We see that with the approach of the molecule AB to the surface a bond is formed between the atom B and the crystal, but this results in rupture of the bond between the atoms A and B. This process, it will be seen, is associated with the surmounting of a certain energy barrier, i.e., requires activation energy. The top of the barrier (on the lower curve in Fig. 1) corresponds to the state ABeL, an unstable intermediate state (the so-called "transition complex"). The bonds present in this state are completely analogous to those present in the molecule H_3.

Surface Radicals

Our problem about the dissociation of the molecule AB is analogous to the well-known problem of Slater [7]. Slater considered three univalent atoms, A, B, and C arranged in a straight line; he investigated the substitution reaction:

$$AB + C \rightarrow A + BC.$$

In our problem the role of the atom C is played by the crystal lattice, considered as a single whole.

We see that in our problem the free lattice electron again plays the part of a free valence. This free valence, wandering over the surface of the crystal, causes the rupture of the valence bond in the AB molecule and becomes saturated by the freed valence. The crystal surface here performs the function of a free radical, and the dissociation reaction occurring on adsorption can be written as an ordinary reaction with participation of a free radical:

$$AB + \dot{L} \rightarrow \dot{A} + BL,$$

in which L, is the lattice and a point over a symbol denotes a free valence.

We consider that the results obtained for a diatomic molecule consisting of two univalent atoms can to a certain extent be generalized to cover the case of any molecule. So that a saturated molecule may enter into strong chemical combination with a surface, it is necessary that a bond uniting two atoms or groups of atoms in the molecule be broken and that the free valence of the molecule so formed become saturated by a free surface valence.

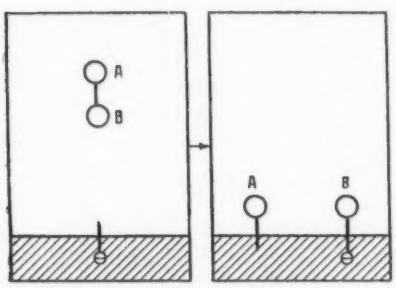

Fig. 2

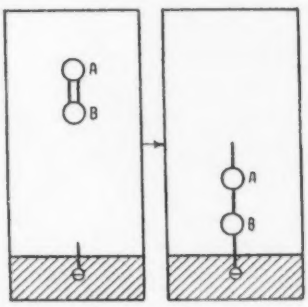

Fig. 3

If in a molecule AB two atoms or groups of atoms, denoted by A and B, are united by a single bond, then rupture of this bond during adsorption results (as we saw in the case of a molecule formed from two univalent atoms) into the dissociation of the molecule into two radicals A and B, the valence of one of which will remain free while the valence of the other becomes saturated with a surface valence, as shown diagrammatically in Fig. 2. In other words, the free lattice electron is brought into play, becomes localized, and pairs off with the lone electron of our radical.

If in the molecule AB the atoms (or groups of atoms) A and B are united not by a single, but by a multiple (e.g. double as in the O_2 molecule) bond, then during adsorption one of these bonds is broken and in this case (unlike the previous one) the act of adsorption is not accompanied by dissociation of the molecule. We obtain a radical AB with one free valence, held on the surface by a lattice electron, as represented in Fig. 3:

$$AB + \dot{L} \rightarrow \dot{A}BL.$$

It should be noted that radicals of this type do not, of course, exist in the gas phase. It should be noted also that such surface radicals are not electrically neutral species, but are associated with an electrical charge, i.e., are ion-radicals.

Hence, on adsorption, a saturated molecule is converted into a radical or is split into two radicals. As we have seen, this occurs as a result of the adsorption act itself.

SUMMARY

In conclusion, let us again ask ourselves the question formulated at the beginning of our paper: why does transfer of reaction from the gas phase to the surface of a semiconductor result in facilitation of the reaction? Answering this question is equivalent to answering the question of what the mechanism of the action of a semiconductor is.

Investigation of the mechanism of chemisorption throws some light on this question. As we have seen, saturated molecules in passing into the chemisorbed state are converted into surface radicals. This in itself chemisorbed state are converted into surface radicals. This in itself increases their reactivity, for radicals are always more reactive than saturated molecules. Hence, the adsorption act itself, with which every heterogeneous catalytic process begins, results in increase in the reactivity of the molecules taking part in the process.

In what then is the specific role of the catalyst?

The transformation of molecules into surface radicals occurs, as we have seen, by the use of free valences of the surface itself. These surface valences therefore play the main part in the direction of the process. The catalyst is the carrier of such free valences. As we have seen, the functions of these free valences are performed by free electrons and holes in the crystal lattice.

Hence, the crystal, taken as a whole, may be regarded as a sort of macroscopic molecule having unsaturated valences; it can be regarded as a sort of "polyradical". The part played by free radicals in the kinetics of homogeneous reactions is well known. The introduction of such radicals into a medium in which reaction is occurring (i.e., the introduction of free valences) causes increase in reaction rate. In the case of catalysis, free valences are introduced by the catalyst itself. The introduction of these free valences stimulates the reaction. We arrive at the concept of the crystalline catalyst as a peculiar kind of "polyradical". We must therefore abandon the long-held view of the existence of a difference in principle between heterogeneous catalysis and the kinetics of homogeneous reactions.

LITERATURE CITED

[1] F. F. Volkenshtein, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1953, 788, 972.

[2] F. F. Volkenshtein, J. Phys. Chem. 27, 159 (1953); 27, 167 (1953).

[3] F. F. Volkenshtein, in the Collection "Problems of Kinetics and Catalysis," Vol. 8, Izd. AN SSSR, 1955, p. 79.*

* In Russian.

[4] F. F. Volkenshtein and V. B. Sandomirsky, loc. cit., 8, 1955, p. 189.

[5] V. V. Voevodsky, F. F. Volkenshtein, and N. N. Semenov, in the Collection "Questions of Chemical Kinetics, Catalysis, and Reactivity," Izd. AN SSSR, 1955, p. 423.*

[6] F. F. Volkenshtein, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1957, 143.

[7] Slater, Phys. Rev. 38, 1109 (1931).

Institute of Physical Chemistry of
the Academy of Sciences of the USSR

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* In Russian.

SYNTHESIS OF ORGANOARSENIC COMPOUNDS OF THE TYPES ArAr'AsX AND ArAr'Ar"As VIA DOUBLE DIAZONIUM SALTS

A. N. Nesmeyanov, O. A. Reutov, Yu. G. Bundel', and I. P. Beletskaya

For the synthesis of disubstituted aromatic arsenic compounds (both symmetrical and mixed) it is usual to use Bart's diazo method [1], the yields, however, being much lower than in the preparation of arenearsonic acids. Symmetrical and mixed triarylarsines may be prepared by the reaction of Michaelis [2, 3] or with the aid of organomagnesium compounds [4, 5].

In the present work on the preparation of compounds of the types ArAr'AsX and ArAr'Ar"As we used the method synthesizing organoarsenic compounds via double diazonium salts [6, 7]. It was found that aryldiiodoarsines react with double diazonium ferric or zinc chlorides in an acetone medium with formation of mixed diarylhaloarsines:

$$ArAsI_2 \xrightarrow[(Ar'N_2Cl)_2 \cdot ZnCl_2]{Ar'N_2Cl \cdot FeCl_3} ArAr'AsX^*$$

The reaction is carried out as follows: the double diazonium salt is added to a stirred cooled solution of the aryldiiodoarsine in acetone at such a rate that the reaction temperature does not rise above 5°. When evolution of nitrogen ceases, the solution is filtered from inorganic precipitate, and solvent is distilled off.

Mixed bisdiarylarsenic oxides $(ArAr'As)_2O$, usually viscous nondistilling oils, were obtained by hydrolysis of the reaction products with aqueous alkali. Oxidation of these with hydrogen peroxide converted them into diarylarsinic acids, and saturation of alcoholic solutions of the oxides with hydrogen chloride converted them into the corresponding chlorides.

We later developed a simpler method for the synthesis of compounds of the type ArAr'AsX: it consisted in the action of sodium iodide on a mixture of the aryldichloroarsine and the double diazonium ferric chloride in an acetone medium:

$$ArAsCl_2 + Ar'N_2Cl \cdot FeCl_3 + NaI \rightarrow ArAr'AsX.$$

By this method we prepared a series of compounds of the type $\begin{matrix} C_6H_5 \\ Ar \end{matrix}\!\!>\!AsX$ which, in addition to phenyl, contained the following radicals: p-nitrophenyl, o-nitrophenyl, o-(methoxycarbonyl)phenyl, p-chlorophenyl, o-carboxyphenyl, o-ethoxyphenyl, p-bromophenyl, p-tolyl, and 2-naphthyl. The yields obtained ranged from 40% to 60%, depending on the radical introduced. Substances obtained by the arylation of dichlorophenylarsine with double diazonium salts are listed in Table 1.

The method developed for the synthesis of mixed diarylhaloarsines is to be preferred to the usual Bart's method for preparing these compounds: diarylhaloarsines are obtained one stage, instead of two stages, and generally in higher yield.

*The formation of a disubstituted organic derivative of tervalent arsenic indicates that, in addition to arylation $ArAsX_2 + Ar'N_2X \cdot MeX_n \rightarrow ArAr'AsX_3 + N_2 + MeX_n$, reduction of the compound $ArAr'AsX_3$ to ArAr'AsX occurs, probably under the action of iodide ions since this reaction is generally accompanied by the liberation of elementary iodine.

The synthesis of mixed triarylarsines of the types $Ar_2Ar'As$ and $ArAr'Ar''As$ was effected by reaction of Ar_2AsCl and $ArAr'AsCl$ in the cold with double diazonium zinc or ferric chlorides in an acetone medium in presence of iron powder.

$$Ar_2AsCl + Ar'N_2Cl \cdot MeCl_n + Fe \rightarrow Ar_2Ar'As + N_2 + FeCl_2 + MeCl_n;$$
$$ArAr'AsCl + Ar''N_2Cl \cdot MeCl_n + Fe \rightarrow ArAr'Ar''As + N_2 + FeCl_2 + MeCl_n.$$

The reactions proceed smoothly in 50-80% yields. The mixed triarylarsines were identified in most cases in the form of mercuric chloride complexes. Table 2 lists substances formed in the arylation of diarylchloroarsines with double diazonium salts.

TABLE 1

Substances Obtained by Arylation of Dichlorophenylarsine by Double Diazonium Ferric and Zinc Chlorides (Decomposition by Sodium Iodide in Acetone)

Expt.	Double salt	Reaction product	Yield %	From in which identified	M. p. (°C)
1	$(C_6H_5N_2Cl)_2 \cdot ZnCl_2$	$(C_6H_5)_2AsO$	54	C_6H_5AsOOH	178
2	$p\text{-}NO_2C_6H_4N_2Cl \cdot FeCl_3$	$C_6H_5(p\text{-}NO_2C_6H_4)AsCl$	40	$C_6H_5(p\text{-}NO_2C_6H_4)AsOOH$	173
3	$o\text{-}NO_2C_6H_4N_2Cl \cdot FeCl_3$	$(C_6H_5)(o\text{-}NO_2C_6H_4)AsO$	72	$C_6H_5(o\text{-}NO_2C_6H_4)AsOOH$	193,5
4	$o\text{-}CH_3OCOC_6H_4N_2Cl \cdot FeCl_3$	$C_6H_5(o\text{-}CH_3OCOC_6H_4)AsCl$	32	$C_6H_5(o\text{-}CH_3OCOC_6H_4)AsOOH$ $C_6H_5(o\text{-}HOOCC_6H_4)AsOOH$	300 with decomposition 300
5	$o\text{-}C_2H_5OC_6H_4N_2Cl \cdot FeCl_3$	$(C_6H_5)(o\text{-}C_2H_5OC_6H_4)AsO$	64	$C_6H_5(o\text{-}C_2H_5OC_6H_4)AsOOH$	182
6	$\beta\text{-}C_{10}H_7N_2Cl \cdot FeCl_3$	$(C_6H_5)(\beta\text{-}C_{10}H_7)AsO$	64	$C_6H_5(\beta\text{-}C_{10}H_7)AsOOH$	156—159
7	$p\text{-}CH_3C_6H_4N_2Cl \cdot FeCl_3$	$C_6H_5(p\text{-}CH_3C_6H_4)AsCl$	37	$C_6H_5(p\text{-}CH_3C_6H_4)AsOOH$	162
8	$(p\text{-}BrC_6H_4N_2Cl)_2 \cdot ZnCl_2$	$C_6H_5(p\text{-}BrC_6H_4)AsCl$	25	$C_6H_5(p\text{-}BrC_6H_4)AsOOH$	176
9	$(p\text{-}ClC_6H_4N_2Cl)_2 \cdot ZnCl_2$	$C_6H_5(p\text{-}ClC_6H_4)AsCl$	39	$C_6H_5(p\text{-}ClC_6H_4)AsOOH$	161—162

The method of synthesis that we have developed makes it possible to prepare mixed triarylarsines containing a greater variety of radicals than is possible in synthesis by the Michaelis method via organomagnesium compounds. The method is simple to carry out.

Until now only a few compounds of the type $ArAr'Ar''As$ were known, and these were prepared by multistage synthesis [8]. With the development of the double diazonium salt method, these compounds are becoming quite accessible.

EXPERIMENTAL

1. Reaction of diiodophenylarsine with double benzenediazonium zinc chloride. A solution of 10 g (0.025 mole) of diiodophenylarsine in 70 ml of acetone was cooled to 0° and stirred while 6.7 g (0.016 mole) of double benzenediazonium zinc chloride was added in such a way that the temperature remained at 0°. When evolution of nitrogen had ceased, the reaction mixture was filtered from inorganic precipitate, which was washed with a small amount of acetone. Solvent was evaporated from the combined filtrates, and the residue, a dark-colored viscous liquid, was washed with three successive 20-ml portions of hydrochloric acid (1 : 1) and hydrolyzed with 30 ml of 40% KOH.

TABLE 2

Substances Formed in the Arylation of Diarylchloroarsines with Double Diazonium Zinc and Ferric Chlorides (Decomposition with Iron in Acetone)

Expt.	Compound to be arylated	Double salt	Reaction product	Yield %	Form in which identified	M. p. (°C)
1	$(C_6H_5)_2AsCl$	$(p\text{-}ClC_6H_4N_2Cl)_2 \cdot ZnCl_2$	$(C_6H_5)_2As(p\text{-}ClC_6H_4)$	64	$(C_6H_5)_2As(p\text{-}ClC_6H_4) \cdot HgCl_2$	177
2	$(C_6H_5)_2AsCl$	$(p\text{-}BrC_6H_4N_2Cl)_2 \cdot ZnCl_2$	$(C_6H_5)_2As(p\text{-}BrC_6H_4)$	81	$(C_6H_5)_2As(p\text{-}BrC_6H_4) \cdot HgCl_2$	172—173
3	$(C_6H_5)_2AsCl$	$p\text{-}CH_3C_6H_4N_2Cl)_2 \cdot ZnCl_2$	$(C_6H_5)_2As(p\text{-}CH_3C_6H_4)$	60	$(C_6H_5)_2As(p\text{-}CH_3C_6H_4)$	48
					$[(C_6H_5)_2As(p\text{-}CH_3C_6H_4)]_2 \cdot HgCl_2$	182—183
4	$(C_6H_5)_2AsCl$	$p\text{-}NO_2C_6H_4N_2Cl \cdot FeCl_3$	$(C_6H_5)_2As(p\text{-}NO_2C_6H_4)$	51	$(C_6H_5)_2As(p\text{-}NO_2C_6H_4)$	109
					$(C_6H_5)_2As(p\text{-}NO_2C_6H_4) \cdot HgCl_2$	145—146
5	$(C_6H_5)_2AsCl$	$o\text{-}CH_3OCOC_6H_4N_2Cl \cdot FeCl_3$	$(C_6H_5)_2As(o\text{-}CH_3OCOC_6H_4)$	73	$(C_6H_5)_2As(o\text{-}CH_3OCOC_6H_4)$	99
					$(C_6H_5)_2As(o\text{-}CH_3OCOC_6H_4) \cdot HgCl_2$	231—232 with decomposition

TABLE 2 (continued)

Expt.	Compound to be arylated	Double salt	Reaction product	Yield %	Form in which identified	M. p. (°C)
6	C_6H_5, $p\text{-}ClC_6H_4$ >AsCl	$(p\text{-}CH_3C_6H_4N_2Cl)_2 \cdot ZnCl_2$	C_6H_5, $p\text{-}ClC_6H_4$, $p\text{-}CH_3C_6H_4$ >As	38	C_6H_5, $p\text{-}ClC_6H_4$, $p\text{-}CH_3C_6H_4$ >As·$HgCl_2$	188—189
7	C_6H_5, $p\text{-}BrC_6H_4$ >AsCl	$(p\text{-}CH_3C_6H_4N_2Cl)_2 \cdot ZnCl_2$	C_6H_5, $p\text{-}BrC_6H_4$, $p\text{-}CH_3C_6H_4$ >As	52	C_6H_5, $p\text{-}BrC_6H_4$, $p\text{-}CH_3C_6H_4$ >As·$HgCl_2$	196—197
8	C_6H_5, $p\text{-}CH_3C_6H_4$ >AsCl	$p\text{-}NO_2C_6H_4N_2Cl \cdot FeCl_3$	C_6H_5, $p\text{-}CH_3C_6H_4$, $p\text{-}NO_2C_6H_4$ >As	42	C_6H_5, $p\text{-}CH_3C_6H_4$, $p\text{-}NO_2C_6H_4$ >As·$HgCl_2$	193—194
9	C_6H_5, $p\text{-}CH_3C_6H_4$ >AsCl	$o\text{-}CH_3OCOC_6H_4N_2Cl \cdot FeCl_3$	C_6H_5, $p\text{-}CH_3C_6H_4$, $o\text{-}CH_3OCOC_6H_4$ >As	52	C_6H_5, $p\text{-}CH_3C_6H_4$, $o\text{-}CH_3OCOC_6H_4$ >As·$HgCl_2$	192
10	C_6H_5, $p\text{-}BrC_6H_4$ >AsCl	$o\text{-}CH_3OCOC_6H_4N_2Cl \cdot FeCl_3$	C_6H_5, $p\text{-}BrC_6H_4$, $o\text{-}CH_3OCOC_6H_4$ >As	79	C_6H_5, $p\text{-}BrC_6H_4$, $o\text{-}CH_3OCOC_6H_4$ >As·$(OH)_2$	212—215

Bisdiphenylarsenic oxide was washed three times with water and then dissolved in ether; the resulting solution was filtered to remove inorganic impurities. After evaporation of ether the oxide gradually crystallized. The yield of bisdiphenylarsenic oxide was 4.1 g (54% on the amount of double salt and 70% on the amount of diiodophenylarsine). After two recrystallizations from petroleum ether it had m.p. 91°; the literature gives m.p. 92.5° [9], m.p. 91-92° [10].

2. Reaction of dichlorophenylarsine with double benzenediazonium zinc chloride in presence of sodium iodide. Double benzenediazonium zinc chloride (9.6 g, i.e., 0.023 mole) was suspended in a solution of 8 g (0.036 mole).of dichlorophenylarsine in 30 ml of acetone. The mixture was cooled to 0° and stirred while a solution of 9 g (0.06 mole) of sodium iodide in 40 ml of acetone was added over a period of 90 minutes. When nitrogen ceased to be evolved, the reaction mixture was filtered from inorganic precipitate, which was washed with a little acetone. Solvent was evaporated from the combined filtrates. The residue, a dark-colored viscous liquid, was washed with three 20 ml portions of 1:1 HCl and hydrolyzed with 30 ml of 40% KOH; the mixture solidified. The bisdiphenylarsenic oxide was washed three times with water and then dissolved in ether, the resulting solution being filtered to remove inorganic impurities. Ether was evaporated. The yield of bisdiphenylarsenic oxide was 4.6 g (42% on the double salt and 54% on dichlorophenylarsine). The oxide was oxidized with 30% hydrogen peroxide to diphenylarsinic acid, m.p. 178° after two recrystallizations from water; the literature gives m.p. 178° [1], m.p. 178° [11].

3. Reaction of dichlorophenylarsine with double p-chlorobenzenediazonium zinc chloride in presence of sodium iodide. Double p-chlorobenzenediazonium zinc chloride (18.8 g, i.e., 0.088 mole) was suspended in a solution of 17.2 g (0.077 mole) of dichlorophenylarsine in 50 ml of acetone. The mixture was cooled to 0° and stirred while a solution of 22.4 g (0.015 mole) of sodium iodide in 50 ml of acetone was added over a period of two hours. When nitrogen ceased to be evolved, the solution was filtered from inorganic precipitate, acetone was evaporated, and the residue was washed with three 20-ml portions of 1:1 HCl and hydrolyzed with 40 ml of 40% KOH. The bis(p-chlorophenylphenylarsenic) oxide was washed with water and dissolved in ethanol. The alcoholic solution was saturated with hydrogen chloride. The oxide was precipitated with dilute hydrochloric acid, extracted with chloroform, and dried over fused calcium chloride. Chloroform was distilled off, and vacuum distillation of the residue gave 5.7 g (39%) of chloro(p-chlorophenyl)phenylarsine, b.p. 180-190° (6 mm) (the literature [8] gives b.p. 176-178° (0.5 mm)).

This chloro compound was oxidized with 30% hydrogen peroxide into (p-chlorophenyl)phenylarsinic acid; the formation of the acid required long heating and was accompanied by solidification. The acid was washed with acetone and recrystallized three times from water; m.p. 161-162° (the literature gives m.p. 162-163° [8] and 189-190° [11]).

Found %: C 47.81, 47.91; H 3.62, 3.51. $C_6H_5(n\text{-}ClC_6H_4)AsO_2H$. Calculated %: C 48.13; H 3.36.

4. Reaction of Dichlorophenylarsine with double p-nitrobenzenediazonium ferric chloride in presence of sodium iodide. Double p-nitrobenzenediazonium ferric chloride (20.27 g, i.e., 0.059 mole) and dichlorophenylarsine (10 g, i.e., 0.045 mole) were dissolved in 30 ml of acetone. The solution was cooled to 0° and stirred while a solution of 13 g (0.09 mole) of sodium iodide in 50 ml of acetone was added over a period of 90 minutes. When evolution of nitrogen ceased, the reaction mixture was filtered from inorganic precipitate, which was washed with acetone. Solvent was evaporated from the combined filtrates, and the residual oil was washed with three 20-ml portions of 1:1 HCl and dissolved in a little chloroform. The chloroform solution was washed with aqueous sodium carbonate solution until it was decolorized. Chloroform was evaporated off, and the residue was hydrolyzed by heating it with 30 ml of 40% KOH. The product was extracted with ether in a Soxhlet. The residue remaining after evaporation of solvent from the ether extract was bis(p-nitrophenylphenylarsenic) oxide (a viscous oil) contaminated with p-nitrobenzenearsonic acid, which was removed by extraction with petroleum ether. After being recrystallized from acetone, p-nitrobenzenearsonic acid melted with decomposition at 300° (the literature [1] gives m.p. 300° with decomposition).

Found %: C 29.00, 29.03; H 1.97, 1.89. $p\text{-}NO_2C_6H_4AsO_3H_2$. Calculated %: C 29.15; H 2.42.

The yield of bis(p-nitrophenylphenylarsenic) oxide was 8.3 g (51.6% on the double salt and 66% on dichlorophenylarsine). It was dissolved in alcohol and the solution was saturated with hydrogen chloride. Chloro-(p-nitrophenyl)phenylarsine was precipitated from solution by addition of 1:1 HCl, separated, and dried with

fused calcium chloride. Vacuum distillation gave 5.6 g (40% on dichlorophenylarsine with 30% on the double salt), b.p. 170-190° (6 mm); the product was oxidized with 30% hydrogen peroxide into (p-nitrophenyl)phenylarsinic acid. The oxidation was carried out hot, and the acid formed dissolved, but separated from solution on cooling. After two recrystallizations from water it melted at 173° (the literature [11] gives m.p. 180°).

Found %: C 46.90, 47.02; H 3.59, 3.43. $(p\text{-}NO_2C_6H_4)C_6H_5AsO_2H$. Calculated %: C 46.90; H 3.22.

5. Reaction of dichlorophenylarsine with double o-Nitrobenzenediazonium ferric chloride in presence of sodium iodide. Reaction was between 20.3 g (0.059 mole) of double o-nitrobenzenediazonium ferric chloride and 10 g (0.045 mole) of dichlorophenylarsine as a solution in 50 ml of acetone. The mixture was cooled to 0° and stirred while a solution of 13 g (0.086 mole) of sodium iodide in 30 ml of acetone was added over a period of 90 minutes. The reaction mixture was treated as described above (Experiments 2-4). Hydrolysis gave bis(o-nitrophenylphenylarsenic) oxide, identified in the form of (o-nitrophenyl)phenylarsinic acid, which, after being washed with acetone and ether and then recrystallized three times from water, had m.p. 193.5° (the literature gives m.p. 196° [12] and m.p. 199° [11]).

Found %: C 46.77, 46.80; H 3.46, 3.59. $(o\text{-}NO_2C_6H_4)C_6H_5AsO_2H$. Calculated %: C 46.90; H 3.22.

Found %: As 24.97, 24.08. $(o\text{-}NO_2C_6H_4)C_6H_5AsO_2H$. Calculated %: As 24.40.

6. Reaction of dichlorophenylarsine with double o-(methoxycarbonyl)benzenediazonium ferric chloride. Double o-(methoxycarbonyl)benzenediazonium ferric chloride (21.1 g, i.e., 0.059 mole) and dichlorophenylarsine (10 g, i.e., 0.045 mole) were dissolved in 30 ml of acetone. The mixture was cooled to 0° and stirred while a solution of 13 g (0.086 mole) of sodium iodide in 40 ml of acetone was added over a period of 90 minutes. The reaction mixture was treated in the usual way. The oil obtained by hydrolysis was washed with water and extracted with ether; solvent was evaporated off. The yield of bis(o-carboxyphenylphenylarsenic) oxide was 6.5 g (50% on the double salt and 65% on dichlorophenylarsine). The oxide was oxidized with 30% hydrogen peroxide into (o-carboxyphenyl)phenylarsinic acid, which decomposed at about 300° after two recrystallizations from water. The literature [11] gives 239° for the decomposition temperature.

Found %: C 51.27, 51.45; H 3.68, 3.65. $(o\text{-}HOOCC_6H_4)C_6H_5AsO_2H$. Calculated %: C 50.99; H 3.62.

Found %: As 25.09, 24.83. $(o\text{-}HOOCC_6H_4)C_6H_5AsO_2H$. Calculated %: As 24.46.

The part of the oil that did not dissolve in ether was dissolved in alcohol, and the solution was filtered from inorganic impurities. Alcohol was evaporated, and the residue of bis(o-carboxyphenylphenylarsenic) oxide amounted to 3.4 g (20% on the double salt and 25.6 %on dichlorophenylarsine). The oxide was oxidized with 30% hydrogen peroxide into (o-carboxyphenyl)phenylarsinic acid. After two reprecipitations by ether from chloroform, its decomposition temperature was above 300°. The substance is colorless, difficultly soluble in water and ether, readily soluble in chloroform.

Found %: C 52.46, 52.64; H 3.31, 3.33. $(o\text{-}CH_3OOCC_6H_4)C_6H_5AsO_2H$. Calculated %: C 52.51; H 4.08.

Found %: As 23.74, 23.61. $(o\text{-}CH_3OOCC_6H_4)C_6H_5AsO_2H$. Calculated %: As 23.40.

This substance is described for the first time.

7. Reaction of dichlorophenylarsine with double o-ethoxybenzenediazonium ferric chloride in presence of sodium iodide. Double o-ethoxybenzenediazonium ferric chloride (21.5 g, i.e., 0.059 mole) and dichlorophenylarsine (10 g, i.e., 0.045 mole) were dissolved in 30 ml of acetone. The mixture was cooled to 0° and stirred while a solution of 13 g (0.086 mole) of sodium iodide in 40 ml of acetone was added over a period of 90 minutes. The reaction mixture was treated in the usual way. After hydrolysis the yield of bis(o-ethoxyphenylphenylarsenic) oxide was 8 g (49% on the double salt and 64% on dichlorophenylarsine). It was converted into (o-ethoxyphenyl)phenylarsinic acid, which was washed with acetone and ether; m.p. 182° after two recrystallizations from water.

Found %: C 55.25, 55.46; H 5.17, 5.28. $(o\text{-}C_2H_5OC_6H_4)C_6H_5AsO_2H$. Calculated %: C 54.93; H 4.94.

Found %: As 24.60, 24.12. $(o\text{-}C_2H_5C_6H_4)C_9H_5AsO_2H$. Calculated %: As 24.46.

The substance is described for the first time.

8. Reaction of dichlorophenylarsine with double 2-naphthalenediazonium ferric chloride in presence of sodium iodide. Double 2-naphthalenediazonium ferric chloride (20.6 g, i.e., 0.059 mole) and dichlorophenylarsine (10 g, i.e., 0.045 mole) were dissolved in 30 ml of acetone. The mixture was cooled to 0° and stirred while a solution of 13 g (0.086 mole) of sodium iodide in acetone was added. The yield of bis-2-naphthylphenylarsenic oxide obtained after treatment of the reaction mixture in the usual way was 8.4 g (49% on the double salt and 63% on dichlorophenylarsine). Oxidation into 2-naphthylphenylarsinic acid proceeded readily and was accompanied by solidification. The acid was washed with acetone; it could not be crystallized from water. After two recrystallizations from benzene it melted at 156-158° (the literature [13] gives m.p. 157-159°).

Found %: As 23.77, 23.88. $(\beta\text{-}C_{10}H_7)C_6H_5AsO_2H$. Calculated %: As 23.99.

9. Reaction of dichlorophenylarsine with double p-toluenediazonium ferric chloride in presence of sodium iodide. Double p-toluenediazonium ferric chloride (18.5 g, i.e., 0.059 mole) and dichlorophenylarsine (10 g, i.e., 0.045 mole) were dissolved in 30 ml of acetone. The mixture was cooled to 0° and stirred while a solution of 13 g (0.086 mole) of sodium iodide in acetone was added. The yield of bisphenyl-p-tolylarsenic oxide obtained after treatment of the reaction mixture in the usual way was 7.6 g (54% on the double salt and 71% on dichlorophenylarsine). The oxide was washed with water and dissolved in alcohol; the alcoholic solution was saturated with hydrogen chloride. Addition of 1:1 HCl precipitated chlorophenyl-p-tolylarsine, contaminated with iodotoluene. The organic layer was separated, dried with fused calcium chloride, and vacuum-distilled. Two fractions were collected: Fraction I, b.p. 80-85° (10 mm), and Fraction II, b.p. 190-225° (18 mm). Fraction I was p-iodotoluene, m.p. 33° (the literature gives b.p. 211.5° (760 mm) and m.p. 34° [14]). Fraction II was chlorophenyl-p-tolylarsine, yield 4.7 g (37% on dichlorophenylarsine and 29% on the double salt). The literature [2] gives b.p. 215-237° (29 mm). For identification purposes this chloro compound was oxidized into phenyl-p-tolylarsinic acid, which melted at 162° after three recrystallizations from water (the literature gives m.p. 159° [11], m.p. 158-160° [2], m.p. 148-150° [9]).

Found %: As 27.45, 27.58. $(p\text{-}CH_3C_6H_4)C_6H_5AsO_2H$. Calculated %: As 27.15.

10. Reaction of dichlorophenylarsine with double p-bromobenzenediazonium zinc chloride in presence of sodium iodide. Double p-bromobenzenediazonium zinc chloride (25.8 g, i.e., 0.045 mole) was suspended in a solution of 20 g (0.089 mole) of dichlorophenylarsine in 60 ml of acetone. The mixture was cooled to 0° and stirred while a solution of 26 g (0.17 mole) of sodium iodide in 80 ml of acetone was added over a period of 2.5 hours. When nitrogen ceased to be evolved, the reaction mixture was filtered from inorganic precipitate, which was washed with a little acetone. Solvent was evaporated from the combined filtrates under the vacuum of a water pump. The residue, a dark-colored viscous liquid, was washed with three 30 ml portions of 1:1 HCl and treated in chloroform solution with aqueous sodium carbonate until it was decolorized. The chloroform was evaporated off, and hydrolysis was effected by addition of alcoholic alkali. Bis(p-bromophenylphenylarsenic) oxide was precipitated with water and then dissolved in alcohol; the alcoholic solution was saturated with hydrogen chloride.

(p-Bromophenyl)chlorophenylarsine was precipitated with dilute HCl and extracted with chloroform; the chloroform extract was dried with fused calcium chloride. Chloroform was distilled off, and vacuum distillation then gave 7 g (25%) of (p-bromophenyl)chlorophenylarsine, b.p. 178-190° (6 mm) (the literature [8] gives b.p. 184-186° (0.3 mm)). This compound was oxidized with 30% hydrogen peroxide into (p-bromophenyl)phenylarsinic acid; during oxidation solidification occurred. The acid was washed with acetone and ether. After two crystallizations from water it melted at 176° (the literature gives m.p. 174-176° [8] and m.p. 184-185° [15]).

11. Reaction of chloro(p-chlorophenyl)phenylarsine with double p-toluenediazonium zinc chloride in presence of iron powder. Double p-toluenediazonium zinc chloride (5.6 g, i.e., 0.012 mole) was suspended in a solution of 5.7 g (0.019 mole) of chloro(p-chlorophenyl)phenylarsine in 20 ml of acetone. The mixture was cooled to 0° and stirred while 1.4 g (0.025 g-atom) of iron powder was added over a period of 40-50 minutes. When nitrogen ceased to be evolved, the solution was filtered from inorganic precipitate. Acetone was

evaporated off, and the residue was washed with three 10-ml portions of 1:1 HCl and dissolved in ethanol. Aqueous 40% KOH was then added dropwise until ferric hydroxide ceased to separate; the hydroxide was filtered off. (p-Chlorophenyl)phenyl-p-tolylarsine was precipitated with dilute hydrochloric acid, extracted with chloroform, and dried with fused calcium chloride; chloroform was evaporated off. The yield of triarylarsine, a viscous oil, was 3.4 g (38% on the chloro(p-chlorophenyl)phenylarsine). The literature describes it as a colorless viscous liquid [8].

When an ethereal solution of the triarylarsine was mixed with a solution of mercuric chloride in dry ether, a precipitate of the complex between these two compounds was formed. After three crystallizations from acetic acid it melted at 188-189°. It was faintly pink in color, soluble in ether, but sparingly soluble in acetone.

Found %: C 36.14, 36.19; H 2.70, 2.56. $\begin{matrix} C_6H_5 \\ p\text{-}CH_3C_6H_4 \\ p\text{-}ClC_6H_4 \end{matrix} \!\!>\!\! As \cdot HgCl_2$. Calculated %: C 36.43; H 2.57.

The substance is described for the first time.

12. Reaction of (p-bromophenyl)chlorophenylarsine with double p-toluenediazonium zinc chloride in presence of iron powder. Double p-toluenediazonium zinc chloride (0.006 mole) was suspended in a solution of 3 g (0.08 mole) of (p-bromophenyl)chlorophenylarsine in 20 ml of acetone. The mixture was cooled to 0° and stirred while 0.6 g (0.012 g-atom) of reduced iron powder was added over a period of 30 minutes. The reaction conditions and the treatment of the reaction mixture were similar to those described above for Experiment 11. The yield of (p-bromophenyl)phenyl-p-tolylarsine was 1.8 g (52% on the (p-bromophenyl)chlorophenylarsine). The triarylarsine was identified in the form of its complex with mercuric chloride. After four crystallizations from glacial acetic acid this melted at 196-197°. It is a colorless substance, moderately soluble in ether and sparingly in acetone.

Found %: C 33.42, 33.47; H 2.37, 2.52. $\begin{matrix} C_6H_5 \\ p\text{-}BtC_6H_4 \\ p\text{-}CH_3C_6H_4 \end{matrix} \!\!>\!\! As \cdot HgCl_2$. Calculated %: C 33.89; H 2.39.

The substance is described for the first time.

13. Reaction of double p-nitrobenzenediazonium ferric chloride with chlorophenyl-p-tolylarsine in presence of iron powder. Iron powder (1 g, i.e., 0.018 g-atom) was added over a period of 30 minutes to a cooled (5°) vigorously stirred solution of 2.5 g (0.009 mole) of double p-nitrobenzenediazonium ferric chloride in 20 ml of acetone. Vigorous decomposition occurred. The treatment of the reaction mixture was as described above. After evaporation of solvent from the chloroform extract, the residue was extracted with ether; the ether was evaporated. The yield of (p-nitrophenyl)phenyl-p-tolylarsine was 1.3 g (42%). The melting point of the complex formed with mercuric chloride was 193-194° after two crystallizations from glacial acetic acid. The substance was pale yellow; it was moderately soluble in acetone and ether.

Found %: C 36.18, 35.86; H 2.51, 2.87. $\begin{matrix} C_6H_5 \\ p\text{-}CH_3C_6H_4 \\ p\text{-}NO_2C_6H_4 \end{matrix} \!\!>\!\! As \cdot HgCl_2$. Calculated %: C 35.83; H 2.53.

The substance is described for the first time.

14. Reaction of double o-(methoxycarbonyl)benzenediazonium ferric chloride with chlorophenyl-p-tolylarsine in presence of iron powder. Iron powder (0.9 g, i.e., 0.016 g-atom) was added over a period of 20 minutes to a cooled (5°) vigorously stirred solution of 2.3 g (0.0082 mole) of chlorophenyl-p-tolylarsine and 4.4 g (0.0082 mole) of double o-(methoxycarbonyl)benzenediazonium ferric chloride in 20 ml of acetone. Vigorous decomposition occurred. The reaction mixture was treated in the usual way. The yield of (o-methoxycarbonylphenyl)phenyl-p-tolylarsine was 1.6 g (52%). The complex with mercuric chloride was prepared by cooling to -20°. After being crystallized from glacial acetic acid it melted at 192°. The substance is moderately soluble in ether.

Found %: C 38.79, 38.87; H 3.13, 3.09. $o\text{-}CH_3OOCC_6H_4-As(C_6H_5)(p\text{-}CH_3C_6H_4)\cdot HgCl_2$. Calculated %: C 38.82; H 2.95.

The substance is described for the first time.

15. Reaction of (p-bromophenyl)chlorophenylarsine with double o-(methoxycarbonyl)benzenediazonium ferric chloride. A solution of 3.3 g (0.0096 mole) of (p-bromophenyl)chlorophenylarsine in 10 ml of acetone was cooled to 0° and added to a cooled (5°) solution of 5.1 g (0.0096 mole) of double o-(methoxycarbonyl)-benzenediazonium ferric chloride in 15 ml of acetone. Shortly after the mixing, vigorous decomposition of the double salt set in with rise in temperature. Most of the double salt decomposed in five minutes in absence of reducing agent. When the evolution of gas slowed down, a little (0.3 g) iron powder was added; slow gas evolution continued further for five minutes. When evolution of gas had ceased, the reaction mixture was filtered from unchanged iron and solvent was evaporated from the filtrate. The remaining semisolid mass was washed with 1:1 HCl, treated with water, and heated to the boil. The organic layer first melted and then solidified completely. The yield of (p-bromophenyl) (o-methoxycarbonylphenyl)phenylarsine dihydroxide was 3.5 g (79%).

The product was a white substance, moderately soluble in acetone, but sparingly in ether. After recrystallization from glacial acetic acid it melted at 212-215°.

Found %: C 50.71, 50.55; H 3.28, 3.32. $p\text{-}BrC_6H_4-As(C_6H_5)(o\text{-}CH_3OCOC_6H_4)(OH)_2$. Calculated %: C 50.34; H 3.79.

16. Reaction of double p-chlorobenzenediazonium zinc chloride with chlorodiphenylarsine in presence of iron powder. Iron powder (2 g, i.e., 0.035 g-atom) was added over a period of 30 minutes to a cooled (0°) vigorously stirred suspension of 8.7 g (0.018 mole) of double p-chlorobenzenediazonium zinc chloride in a solution of 7 g (0.026 mole) of chlorodiphenylarsine in 40 ml of acetone. When gas ceased to be evolved, the mixture was filtered from inorganic precipitate, which was washed with acetone. Solvent from the combined filtrates was distilled off under the vacuum of a water pump. The residual viscous liquid was washed with 1:1 HCl and dissolved in alcohol; addition of 40% KOH then precipitated ferric hydroxide. The inorganic precipitate was filtered off, and the triarylarsine was precipitated from solution by addition of dilute HCl. The organic layer (a heavy oil) was separated and dried with fused calcium chloride. Vacuum distillation gave 7 g (62% on chlorodiphenylarsine) of (p-chlorophenyl)diphenylarsine, b.p. 225-230° (6 mm). By mixing ethereal solutions of the triarylarsine and mercuric chloride we prepared the mercuric chloride complex of (p-chlorophenyl)diphenylarsine, m.p. 178° after two crystallizations from acetic acid.

Found %: C 35.43, 35.01; H 2.47, 2.38. $(C_6H_5)_2(p\text{-}ClC_6H_4)As\cdot HgCl_2$. Calculated %: C 35.32; H 2.38.

The substance is described for the first time.

17. Reaction of double p-bromobenzenediazonium zinc chloride with chlorodiphenylarsine in presence of iron powder. Iron powder (2 g, i.e., 0.035 g-atom) was added over a period of one hour to a cooled (0°) vigorously stirred suspension of 10.2 g (0.019 mole) of double p-bromobenzenediazonium zinc chloride in a solution of 7 g (0.026 mole) of chlorodiphenylarsine in 40 ml of acetone. After the usual treatment of the reaction mixture, the triarylarsine was extracted with chloroform and the chloroform was evaporated off. The yield of (p-bromophenyl)diphenylarsine, obtained as a noncrystallizing oil, was 8 g (81% on the chlorodiphenylarsine). The mercuric chloride complex was prepared in the usual way. After crystallization from glacial acetic acid it had m.p. 172-173° (the literature [16] gives m.p. 175-176°).

Found %: C 33.18, 33.18; H 2.25, 2.31. $(C_6H_5)_2(p\text{-}BrC_6H_4)As\cdot HgCl_2$. Calculated %: C 32.94; H 2.15.

18. Reaction of double p-toluenediazonium zinc chloride with chlorodiphenylarsine in presence of iron powder. Iron powder (2 g, i.e., 0.035 g-atom) was added over a period of 90 minutes to a cooled (5°) vigorously stirred suspension of 7.9 g (0.018 mole) of double p-toluenediazonium zinc chloride in a solution of 7 g (0.026 mole) of chlorodiphenylarsine in 40 ml of acetone. When all the iron had been added, the reaction mixture was heated to 30°. When evolution of gas ceased, the reaction mixture was filtered from inorganic precipitate, which was washed with acetone. Solvent from the combined filtrates was driven off at the pump. The residue was washed with 1:1 HCl, and the organic layer was separated. Purification of the reaction product was carried out by the above-described method (Experiment 11). The yield of diphenyl-p-tolylarsine was 5.1 g (60% on the chlorodiphenylarsine). It was obtained as a viscous oil, which dissolved in alcohol when warmed slightly. When the resulting solution was allowed to stand for two weeks, the triarylarsine separated in the crystalline form: m.p. 48°. The literature [2] states that the substance, which is very difficult to crystallize, melts at 50°.

Ethereal mercuric chloride was added to an ethereal solution of the triarylarsine until white precipitate ceased to form. The mercuric chloride complex of diphenyl-p-tolylarsine was crystallized from glacial acetic acid: m.p. 182-183°. It is a white substance, sparingly soluble in ether, but moderately in alcohol.

Found %: C 49.71, 49.90; H 3.66, 3.53. $\left[\begin{matrix} (C_6H_5)_2 \\ p\text{-}CH_3C_6H_4 \end{matrix} \!\!>\!\!= As \right]_2 \cdot HgCl_2$. Calculated %: C 50.05; H 3.75.

19. Reaction of double p-nitrobenzenediazonium ferric chloride with chlorodiphenylarsine in presence of iron powder. Iron powder (1.5 g, i.e., 0.026 g-atom) was added over a period of 40 minutes to a cooled (-5°) vigorously stirred solution of 8.8 g (0.025 mole) of double p-nitrobenzenediazonium ferric chloride and 5 g (0.019 mole) of chlorodiphenylarsine in 30 ml of acetone. Vigorous decomposition occurred. The reaction mixture was treated in the way described above. When solvent was driven off, the residue solidified and was washed with 1:1 HCl. The yield of (p-nitrophenyl)diphenylarsine was 3.4 g (51% on the chlorodiphenylarsine). After two crystallizations from ethanol it melted at 109°. The product was a pale-yellow substance, readily soluble in ether, sparingly in cold alcohol.

Found %: C 60.89, 61.09; H 4.28, 4.29. $\begin{matrix} (C_6H_5)_2 \\ p\text{-}NO_2C_6H_4 \end{matrix} \!\!>\!\!= As$. Calculated %: C 61.58; H 4.02.

Found %: N 4.26, 4.26. $\begin{matrix} (C_6H_5)_2 \\ p\text{-}NO_2C_6H_4 \end{matrix} \!\!>\!\!= As$. Calculated %: N 4.00.

The substance is described for the first time.

Mixing of ethereal solutions of the triarylarsine and mercuric chloride gave the mercuric chloride complex of (p-nitrophenyl)diphenylarsine. After crystallization from glacial acetic acid it melted at 145-146°. It was a pale-yellow substance, moderately soluble in acetone, but sparingly in ether.

Found %: C 34.40, 34.47; H 2.50, 2.52. $\begin{matrix} (C_6H_5)_2 \\ p\text{-}NO_2C_6H_4 \end{matrix} \!\!>\!\!= As \cdot HgCl_2$. Calculated %: C 34.72; H 2.27.

The substance is described for the first time.

20. Reaction of double o-(methoxycarbonyl)benzenediazonium ferric chloride with chlorodiphenylarsine in presence of iron powder. Iron powder (1.5 g, i.e., 0.026 g-atom) was added over a period of 40 minutes to a cooled (-5°) vigorously stirred solution of 5 g (0.019 mole) of chlorodiphenylarsine and 9.1 g (0.025 mole) of double o-(methoxycarbonyl)benzenediazonium ferric chloride in 30 ml of acetone. Vigorous decomposition occurred. The reaction mixture was treated in the way described above. After removal of solvent the residue solidified; it was washed with 1:1 HCl. The yield of (o-methoxycarbonylphenyl)diphenylarsine was 5 g (73% on the chlorodiphenylarsine). After two crystallizations from alcohol it melted at 92°. The substance was colorless, readily soluble in acetone, moderately in ether.

Found %: C 66.13; H 4.86. $(C_6H_5)_2$ \\ o-$CH_3OOCC_6H_4$ / As. Calculated %: C 65.94; H 4.70.

The substance is described for the first time.

After recrystallization from glacial acetic acid the mercuric chloride complex melted with decomposition at 231-232°. The complex was a white substance, slightly soluble in most organic solvents.

Found %: C 37.93, 38.05; H 2.87, 2.91. $(C_6H_5)_2$ \\ o-$CH_3OOCC_6H_4$ / As · $HgCl_2$. Calculated %: C 37.79; H 2.70.

The substance is described for the first time.

SUMMARY

1. A method was developed for the synthesis of mixed organoarsenic compounds of the type ArAr'AsX. In consists in the action of sodium iodide on a mixture of an aryldichloroarsine and a double diazonium ferric or zinc chloride ($ArN_2Cl \cdot FeCl_3$ or $(ArN_2Cl)_2 \cdot ZnCl_2$) in an acetone medium in the cold. Yields of 40-60% were obtained.

2. A method was developed for the synthesis in 50-80 yield of triarylarsines of the type ArAr'Ar"As. It consists in reaction of mixed diarylchloroarsines ArAr'AsCl with double diazonium zinc or ferric chlorides in the cold in an acetone medium in presence of iron powder.

LITERATURE CITED

[1] H. Bart, Ann. 429, 55, 103 (1922).

[2] A. Michaelis, Ann. 321, 155 (1902).

[3] A. Michaelis, Ber., 15, 2876 (1882).

[4] P. Pfeiffer, Ber. 77, 4620 (1904).

[5] F. F. Blicke, and T. D. Smith, J. Am. Chem. Soc. 51, 3479 (1929).

[6] A. N. Nesmeyanov, Prog. Chem. 4, 272 (1945).

[7] O. A. Reutov and Yu. G. Bundel, J. Moscow State Univ. No. 8, 85 (1955); J. Gen. Chem. 25, 2324 (1955).*

[8] F. G. Mann, and J. Watson, J. Chem. Soc. 1947, 505.

[9] F. F. Blicke, and T. D. Smith, J. Am. Chem. Soc. 51, 1558 (1929).

[10] A. Michaelis, and W. La. Coste, Ber. 11 (B), 1887 (1878).

[11] K. Takahashi, J. Pharm. Soc. Japan 72, 523 (1952); Chem. Abstr. 46, 9790 (1952).

[12] E. Sakellarios, Ber. 57 (B), 1514 (1924).

[13] L. Goldsworthy, J. Chem. Soc. 1937, 59, 534.

[14] W. Körner, Z. Chem. 1868, 327.

[15] F. F. Blicke, and G. L. Webster, J. Am. Chem. Soc. 59, 534 (1937).

[16] F. F. Blicke, and E. L. Kataline, J. Am. Chem. Soc. 60, 419 (1938).

M. V. Lomonosov State University
Moscow

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ADDITION OF MERCURY SALTS TO VINYL ETHERS AND ESTERS IN AN ALCOHOLIC MEDIUM

A. N. Nesmeyanov, I. F. Lutsenko, and R. M. Khomutov

In our first paper [1], which reported work on the reaction of mercuric acetate with vinyl ethers, we pointed out that the addition of a mercury salt to a vinyl ether proceeds extremely readily, not only in an aqueous medium, but also in alcohol. When an equivalent amount of an aqueous solution of potassium chloride was added to the reaction product and the mixture was diluted with water, a heavy oil was precipitated, but rapidly decomposed with separation of a white crystalline precipitate. After several hours the oil was completely converted into a solid substance, which was found to be (chloromercuri)acetaldehyde. We suggested that the oily mercury compound was the acetal of (chloromercuri)acetaldehyde.

The formation of an acetal of mercurated acetaldehyde can be represented as follows:

$$CH_2=CHOC_2H_5+(CH_3COO)_2Hg+C_2H_5OH\rightarrow \begin{matrix} CH_3COOHgCH_2CH(OC_2H_5)_2+CH_3COOH \\ \downarrow KCl \\ ClHgCH_2CH(OC_2H_5)_2 \end{matrix}$$

At that time we did not succeed in preparing the acetal in an analytically pure state, owing to the high tendency for decomposition. Later, in a more detailed study of the conditions of formation and the reactions of mercury derivatives of carbonyl compounds, the reasons for the instability of mercurated acetals became clear.

As the above equation shows, in the formation of the mercurated acetal acetic acid is liberated. It was found that the mercurated acetal is so readily hydrolyzed that even dilute aqueous acetic acid brings about this reaction. Hence, in order that the acetal formed in the reaction of mercuric acetate with the pure vinyl ether should not decompose it is necessary to bind the acetic acid liberated. This is effected very simply by taking a mixture of 1 mole of mercuric acetate and 1 mole of mercuric oxide for reaction with 2 moles of vinyl ether. In this case the overall reaction can be represented as follows:

$$2CH_2=CHOR+(CH_3COO)_2Hg+HgO+2ROH\rightarrow 2CH_3COOHgCH_2CH(OR)_2+H_2O$$

$$CH_3COOHgCH_2CH(OR)_2\xrightarrow{Cl'}ClHgCH_2CH(OR)_2.$$

In order that reaction proceed in one way only and lead only to the acetal of mercurated formaldehyde, it must be carried out as follows. The vinyl ether (2 moles) is added in one portion to a mixture of 1 mole of mercuric acetate and absolute alcohol. In this case alcoholysis of the mercury salt first occurs with liberation of acetic acid, and the $CH_3COOHgOR$ formed adds to the vinyl ether with formation of the mercurated acetal:

$$CH_2=CHOR+CH_3COOHgOR\rightarrow CH_3COOHgCH_2CH(OR)_2$$

If mercuric oxide is now added gradually in small portions to the reaction mixture (so that there is always some free acetic acid in the reaction medium), it will react with the acetic acid liberated with formation of more mercuric acetate, which will be alcoholyzed in its turn with formation of $CH_3COOHgOR$.

Hence, when reaction is carried out in this way, the only final product will be the acetal of mercurated acetaldehyde. Verification showed that this variant of the procedure did indeed give a stable acetal of

mercurated acetaldehyde of adequate analytical purity in high yield. When, however, the mercuric oxide was added in one portion, a mixture of addition products of various structure was obtained. In this way we synthesized (chloromercuri)acetaldehyde diethyl acetal and (bromomercuri)acetaldehyde dibutyl acetal.

Acetals of mercurated aldehydes can be prepared also from enol acetates of aldehydes, which in alcoholic solution react readily with mercuric oxide in presence of mercuric acetate. The peculiar feature of this reaction is that here one need take only a small amount of mercuric acetate (10-15 moles % on the amount of enol acetate), since acetic acid is formed in the addition process not only by alcoholysis of mercuric acetate, but also by alcoholysis of the primary addition product formed by $CH_3COOHgOR$ with the enol acetate of the aldehyde:

$$(CH_3COO)_2Hg + ROH \rightarrow CH_3COOHgOR + CH_3COOH$$

$$CH_2=CHOCOCH_3 + CH_3COOHgOR \rightarrow \left[CH_3COOHgCH_2CH(OCOCH_3)(OR) \right] \xrightarrow{ROH} CH_3COOHgCH_2CH(OR)_2 + CH_3COOH.$$

Hence, acetic acid will be formed as reaction proceeds with the enol acetate of the aldehyde, and the initial small amount of mercuric acetate is necessary only for the start of the reaction. By adding mercuric oxide gradually in small portions, we may convert all of the enol acetate of the aldehyde into the acetal of the mercurated aldehyde. In this case, unlike that of reaction with vinyl ethers, after addition of mercuric oxide (85-90 moles %) equivalent to the amount of the enol acetate of the aldehyde taken for reaction medium will contain a little free acetic acid (as a result of the initial presence of mercuric acetate), which must be neutralized in order to avoid hydrolysis of the acetal grouping. With this object the necessary amount of sodium carbonate is added to the aqueous solution of halide into which the reaction mixture is poured in order to precipitate the (halomercuri)acetaldehyde acetal.

By this reaction, starting with vinyl acetate and mercuric oxide (with addition of a little mercuric acetate), we synthesized the dimethyl and diethyl acetals of (chloromercuri)acetaldehyde. (Halomercuri)acetaldehyde acetals are heavy oils, insoluble in water, but fairly readily soluble in organic solvents, including ether. In absence of acids they are fairly stable, but they are readily hydrolyzed even in weakly acid solutions. They are completely decomposed when attempts are made to distill them under reduced pressure.

We succeeded in preparing a crystalline acetal of mercurated acetaldehyde from phenyl vinyl ether. When this was heated with N,N'-mercuribisacetamide and phenol in dichloroethane, the diphenyl acetal of (acetamidomercuri)acetaldehyde was formed:

$$CH_2=CHOC_6H_5 + (CH_3CONH)_2Hg + C_6H_5OH \rightarrow$$
$$\rightarrow CH_3CONHHgCH_2CH(OC_6H_5)_2 + CH_3CONH_2.$$

By double decomposition, reaction between (acetamidomercuri)acetaldehyde diphenyl acetal and mercuric acetate gave (acetoxymercuri)acetaldehyde diphenyl acetal.

In the synthesis of the full organomercury derivatives of ketones and, particularly, aldehydes from mercuric oxide and vinyl ethers [2], small amounts of metallic mercury are always formed in the reaction mixture as a result of oxidative side reactions. In the preparation of small amounts of mercury compounds the metallic mercury can be readily removed by filtration. However, in the preparation of mercuridiacetaldehyde on the large scale we met the following difficulty: in the filtration of the reaction solution, mercuridiacetaldehyde began to crystallize out on the filter. Attempts to recrystallize any appreciable amount of mercuridiacetaldehyde resulted only in contamination of the product. This behavior is associated with the high instability of mercuridiacetaldehyde to heat: in spite of the fact that it has a melting point of 93-95°, heating to 45-50° in a solvent leads to considerable decomposition of the substance.

For the preparation of large amounts of mercuridiacetaldehyde of high purity, we first prepared it in the form of its acetal in an alcoholic medium, filtered off all impurities, and hydrolyzed it in ethereal-alcoholic solution with a little 0.1 N sulfuric acid. By this variant of the method 0.5 mole and more of pure mercuridiacetaldehyde may be readily and rapidly prepared. For each 0.5 mole of mercuric oxide introduced into the reaction it is sufficient to add 4 g of mercuric acetate for initiation of reaction. The reaction that then occurs can be represented as follows:

$$CH_2=CHOR + (CH_3COO)_2Hg + ROH \rightarrow CH_3COOHgCH_2CH(OR)_2 + CH_3COOH.$$

The amount of the acetal of mercurated acetaldehyde formed is only small, being equivalent to the amount of mercuric acetate introduced. The main direction of reaction is as follows:

$$CH_3COOH + HgO \rightarrow CH_3COOHgOH$$

$$CH_2=CHOR + CH_3COOHgOH \rightarrow CH_3COOHgCH_2CH\begin{matrix}\diagup OR\\ \diagdown OH\end{matrix}$$

As a result we obtain a hemiacetal of mercurated acetaldehyde, which undergoes partial alcoholysis in an alcoholic medium:

$$CH_3COOHgCH_2CH\begin{matrix}\diagup OR\\ \diagdown OH\end{matrix} + ROH \rightleftarrows ROHgCH_2CH\begin{matrix}\diagup OR\\ \diagdown OH\end{matrix} + CH_3COOH$$

The acetic acid reacts with mercuric oxide with formation of the basic salt, which yields more of the hemiacetal of mercurated acetaldehyde, and the alkylated organomercury base reacts with the vinyl ether with formation of a partial acetal of mercuridiacetaldehyde:

$$CH_2=CHOR + ROHgCH_2CH\begin{matrix}\diagup OR\\ \diagdown OH\end{matrix} \rightarrow (RO)_2CHCH_2HgCH_2CH\begin{matrix}\diagup OR\\ \diagdown OH\end{matrix}$$

This derivative of mercuridiacetaldehyde is stable for a long time in alcoholic solution and can be filtered from metallic mercury without difficulty. Addition of a few milliliters of 0.1 N H_2SO_4 brings about hydrolysis, and pure mercuridiacetaldehyde is precipitated in high yield. The structure of the partial acetal of mercuridiacetaldehyde was confirmed not only by closely agreeing analyses, but also by the bromination reaction. In the bromination of this compound we obtained almost equal amounts of bromoacetaldehyde acetal and of bromoacetaldehyde itself, whereas in the bromination of acetals of mercurated acetaldehyde we have never observed the formation of bromoacetaldehyde.

In their chemical reactions mercurated acetals are in many ways reminiscent of the addition products formed by mercury salts with olefins. Thus, in the bromination of acetals of mercurated acetaldehyde, acetals of bromoacetaldehyde are formed,

$$XHgCH_2CH(OR)_2 + Br_2 \rightarrow BrCH_2CH(OR)_2 + HgBrX,$$

which indicates the presence of a mercury-carbon bond.

On the other hand, alcoholic potassium iodide breaks down an acetal of mercurated acetaldehyde with formation of an alkyl vinyl ether:

$$XHgCH_2CH(OR)_2 + 4KI \rightarrow CH_2 = CHOR + K_2HgI_4 + ROK + KX.$$

A vinyl ether is obtained also by the action of benzoyl chloride on (chloromercuri)acetaldehyde diethyl acetal:

$$ClHgCH_2CH(OC_2H_5)_2 + C_6H_5COCl \rightarrow CH_2 = CHOC_2H_5 + C_6H_5COOC_2H_5 + HgCl_2.$$

This result is readily explained by the enhanced polarizability of C–Hg and C–O bonds in positions favorable for conjugation (σ-conjugation). Owing to such conjugation, in the electrophilic attack of an oxygen atom of the acetal by the benzoyl group, a $C_2H_5O^-$ anion breaks away and the residue $ClHg^+$ moves away as a cation.

The course of reaction between acetals (including ketals) and benzoyl chloride is completely analogous [3, 4]. However, in the case of the C–H bond cunjugation is much less marked than in the case of the C–Hg bond, so that reaction requires more severe conditions and gives not the vinyl ether, but the α-chloro ether:

$$CH_3CH(OR)_2 + ArCOCl \rightarrow CH_3CHClOR + ArCOOR.$$

EXPERIMENTAL

Preparation of (Chloromercuri)acetaldehyde diethyl acetal from ethyl vinyl ether. Ethyl vinyl ether (7.5 g, i.e., 0.1 mole) was added to a stirred cooled mixture of 15.9 g (0.05 mole) of mercuric acetate and 20 ml of absolute ethanol. When the addition reaction between the mercury salt and the vinyl ether was complete, 10.8 g (0.05 mole) of dry yellow mercuric oxide was added in portions, each of about 1 g, each new portion being added when the previous one dissolved. The reaction mixture was then poured into a solution of 7.5 g (0.1 mole) of potassium chloride in 60 ml of water. A heavy oil separated and was dissolved in 100 ml of ether. The solution was dried with calcium chloride and filtered. Ether and alcohol were distilled off under reduced pressure, and the residue was dried in a vacuum desiccator over phosphoric oxide. In this way we obtained 26 g (73%) of (chloromercuri)acetaldehyde diethyl acetal in the form of a colorless heavy oil.

Found %: Hg 57.15, 57.28. $ClHgCH_2CH(OC_2H_5)_2$. Calculated %: Hg 56.8.

Preparation of (Bromomercuri)acetaldehyde dibutyl acetal from butyl vinyl ether. Butyl vinyl ether (10 g, i.e., 0.1 mole) was added to a well-stirred mixture of 15.9 g (0.05 mole) of mercuric acetate and 15 g of absolute butyl alcohol. When the addition reaction was complete, 10.8 g (0.05 mole) of dry yellow mercuric oxide was added in small portions. The reaction mixture was then poured into a solution of 12 g (0.1 mole) of potassium bromide in 50 ml of water; the oil that separated as a lower layer was removed and was treated as in the preceding experiment. The yield of the dibutyl acetal was 30 g (70%). The compound was a heavy colorless oil.

Found %: Hg 44.78, 44.94. $BrHgCH_2CH(OC_4H_9)_2$. Calculated %: Hg 44.21.

Hydrolysis of (Bromomercuri)acetaldehyde dibutyl acetal. A mixture of 2.8 g of (bromomercuri)acetaldehyde dibutyl acetal and 10 ml of 50% alcohol acidified with a few drops of 0.1 N H_2SO_4 was set aside at room temperature for one day. The crystals of (bromomercuri)acetaldehyde that formed were separated, washed with cold water, and dried; yield 1.8 g (90%); m.p. 138° (from water). In admixture with (bromomercuri)acetaldehyde prepared from vinyl acetate there was no depression of melting point.

Preparation of (Chloromercuri)acetaldehyde diethyl acetal from vinyl acetate. Vinyl acetate (9 g, i.e., 0.1 mole) was added to a mixture of 4.8 g (0.015 mole) of mercuric acetate and 25 ml of absolute ethanol, and the mixture was stirred vigorously while 18.4 g (0.085 mole) of dry yellow mercuric oxide was added in portions of 0.5-1 g. When the mercuric oxide had dissolved, the reaction mixture was poured into a solution of 7.5 g (0.1 mole) of potassium chloride and 1 g of sodium carbonate in 60 ml of water. The lower layer was separated and treated as in the preceding experiment. The yield of (chloromercuri)acetaldehyde was 25 g (70%).

Found %: Hg 56.71, 57.08. $ClHgCH_2CH(OC_2H_5)_2$. Calculated %: Hg 56.80.

Hydrolysis of (Chloromercuri)acetaldehyde diethyl acetal. Water (10 ml) was added to 5.2 g of (chloromercuri)acetaldehyde diethyl acetal, and the mixture was acidified with a few drops of 0.1 N H_2SO_4. After

12 hours crystals of (chloromercuri)acetaldehyde were separated, washed with cold water, and dried: yield 3.8 g (92%). After being recrystallized from water it melted at 129-130°. In admixture with (chloromercuri)acetaldehyde obtained from vinyl acetate there was no depression of melting point.

Preparation of (Acetamidomercuri)acetaldehyde diphenyl acetal. A mixture of 1.6 g of mercuribisacetamide, 1.2 g of phenyl vinyl ether, 1 g of phenol, and 5 ml of dichloroethane was heated carefully until solution was complete. The mixture was set aside at room temperature for one day, after which 15 ml of dry ether was added and the mixture was stirred and cooled strongly. The crystalline precipitate that formed was filtered off at the pump and washed with cold ether. The yield of (acetamidomercuri)acetaldehyde diphenyl acetal was 87%. After being crystallized from carbon tetrachloride it melted at 107-109°.

Found %: C 40.81, 40.66; H 4.12, 3.96. $CH_3CONHHgCH_2CH(OC_6H_5)_2$. Calculated %: C 40.70; H 3.64.

Preparation of (Acetoxymercuri)acetaldehyde diphenyl acetal. Mercuric acetate (0.8 g) was added to a solution of 1.5 g of (acetamidomercuri)acetaldehyde diphenyl acetal in 3 ml of alcohol. The mixture was heated until a clear solution had formed. When the solution was cooled, crystals of (acetoxymercuri)acetaldehyde diphenyl acetal were precipitated; the yield was quantitative. After being recrystallized from alcohol the substance melted at 101-102°.

Found %: Hg 43.02, 42.72. $CH_3COOHgCH_2CH(OC_6H_5)_2$. Calculated %: Hg 42.42.

Bromination of (Chloromercuri)acetaldehyde diethyl acetal. A solution of 12 g of bromine in 30 ml of chloroform was added dropwise to a cooled stirred solution of 26 g (chloromercuri)acetaldehyde diethyl acetal in 50 ml of dry chloroform. A few minutes after the addition of bromine, precipitated mercury salt was filtered off and washed with chloroform. Solvent was distilled from the combined filtrates, and distillation of the residue gave 11.2 g (80%) of bromoacetaldehyde diethyl acetal, b.p. 45-56° (10 mm); n_D^{20} 1.4405; d_4^{20} 1.2853; found MR 40.41; calculated for $C_6H_{13}O_2Br$ MR 40.96. The literature [5] gives b.p. 67° (15 mm); n_D^{20} 1.4401; d_4^{20} 1.286.

Bromination of (Bromomercuri)acetaldehyde dibutyl acetal. When brominated under similar conditions, 22.7 g (bromomercuri)acetaldehyde dibutyl acetal gave 12 g (95%) of bromoacetaldehyde dibutyl acetal, b.p. 88-90° (2 mm); n_D^{20} 1.4475; d_4^{20} 1.1505; MR 59.06; calculated for $C_{10}H_{21}O_2Br$ MR 59.43. The literature [6] gives b.p. 86.5° (1 mm); n_D^{20} 1.44077; d_4^{20} 1.1511.

Reaction of (Chloromercuri)acetaldehyde dimethyl acetal with potassium iodide. A solution of 8 g (0.025 mole) of (chloromercuri)acetaldehyde dimethyl acetal in an equal volume of alcohol was added to a strongly cooled solution of 16.6 g (0.1 mole) of potassium iodide in alcohol. The reaction mixture was heated carefully, and the methyl vinyl ether liberated was passed through a wash bottle containing 10% NaOH solution and absorbed in an aqueous-alcoholic solution of mercuric acetate. When reaction was complete and equivalent amount of potassium chloride solution was added, and the crystals of (chloromercuri)acetaldehyde were separated; yield 3.5 g (50%); m. p. 128-129° (from water).

Reaction of (Chloromercuri)acetaldehyde diethyl acetal with benzoyl chloride. A solution of 21 g (0.15 mole) of benzoyl chloride in benzene was added to a cooled stirred solution of 50 g (0.14 mole) of (chloromercuri)acetaldehyde diethyl acetal in a mixture of 100 ml of benzene and 12 g of pyridine. Stirring was continued for one hour at room temperature, after which a fraction of b.p. 35-40° (4.5 g) was distilled from the reaction mixture. After redistillation the yield of ethyl vinyl ether was 3.6 g (35%); b.p. 35-36°, n_D^{20} 1.3782; d_4^{20} 0.7564; found MR 21.96; calculated C_4H_8O MR 21.85.

Preparation of a Partial Acetal of Mercuridiacetaldehyde. A mixture of 5.4 g (0.025 mole) of dry yellow mercuric oxide, 4 g (0.055 mole) of ethyl vinyl ether, 15 ml of absolute ethanol, and 15 mg of mercuric acetate was shaken until the mercuric oxide dissolved. The reaction mixture was then filtered, and alcohol was distilled off under reduced pressure at 30°. The residue was dissolved in isopentane, the solution was filtered, isopentane was distilled off, and the residue was dried over phosphoric oxide in a vacuum desiccator. The partial acetal of mercuridiacetaldehyde, amounting to 8 g (80%), was obtained in the form of a colorless oil.

Found %: H 49.54, 49.72. $(C_2H_5O)_2CHCH_2HgCH_2CH\begin{matrix}OC_2H_5\\OH\end{matrix}$. Calculated %: H 49.38.

Bromination of the partial acetal of mercuridiacetaldehyde. A solution of 16 g (0.1 mole) of bromine in 30 ml of chloroform was added dropwise to a cooled stirred solution of 20 g (0.05 mole) of the partial acetal of mercuridiacetaldehyde in 50 ml of dry chloroform. The precipitate was filtered off at the pump and washed with chloroform. Solvent distilled from the combined filtrates, and distillation of the residue gave a) bromoacetaldehyde, yield 3.6 g (60%), b.p. 107-112°; n_D^{20} 1.4790; d_4^{20} 1.8410; found MR 18.94; calculated for $BrCH_2CHO$ MR 19.21; b) bromoacetaldehyde diethyl acetal, yield 7 g (71%), b.p. 57-59° (9 mm); n_D^{20} 1.4410; d_4^{20} 1.2865; found MR 40.42; calculated for $BrCH_2CH(OC_2H_5)_2$ MR 40.96. The literature [5] gives b.p. 67° (15 mm), n_D^{20} 1.4401; d_4^{20} 1.286.

Preparation of mercuridiacetaldehyde via the acetal. Butyl vinyl ether (110 g, i.e., 1.1 mole) was added to a cooled vigorously stirred mixture of 108 g (0.5 mole) of dry yellow mercuric oxide, 4 g of mercuric acetate, and 70 ml of absolute methanol. When the mercuric oxide had dissolved, the reaction mixture was filtered and 50 ml of dry ether was added to the filtrate. The mixture was then cooled, and 15 ml of 0.1 N H_2SO_4 was then stirred in. After a short period of standing, the crystalline precipitate formed was separated, washed with a little cold alcohol and then with dry ether, and dried. The yield of mercuridiacetaldehyde, m.p. 92-94° was 121 g (84%). In admixture with authentic mercuridiacetaldehyde there was no depression of melting point.

SUMMARY

1. A method is proposed for the synthesis of acetals of mercurated acetaldehyde from vinyl ethers and esters.

2. It is shown that, in their reactions, mercurated acetals are in many ways reminiscent of the addition products formed by mercury salts with olefins.

LITERATURE CITED

[1] A. N. Nesmeyanov, I. F. Lutsenko, and N. N. Vereshchagina, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1947, 63.

[2] I. F. Lutsenko and R. M. Khomutov, Proc. Acad. Sci. USSR 102, 97 (1955).

[3] E. Blaise, Compt. rend. 139, 1211 (1904); 140, 661 (1955); H. Post, J. Org. Chem. 1, 236 (1936).

[4] O. Grummit, and J. Stearus, J. Am. Chem. Soc. 77, 3136 (1955).

[5] E. Marvell, and M. Joncich, J. Am. Chem. Soc. 73, 973 (1951).

[6] T. Jacobs, R. Cramer, and J. Hanson, J. Am. Chem. Soc. 64, 223 (1942).

M. V. Lomonosov State University
Moscow

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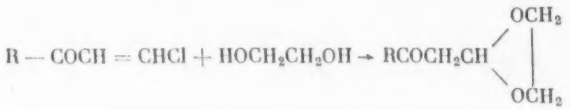
CYCLIC ACETALS OF β-KETO ALDEHYDES AND THEIR USE IN THE SYNTHESIS OF ALKYLNAPHTHALENES

N. K. Kochetkov, E. E. Nifantyev, and A. N. Nesmeyanov

It is known that reaction of alkyl 2-chlorovinyl ketones with alcohols gives acetals of β-keto aldehydes [1-3]. These reactive compounds are of great interest for organic synthesis and have already found application in the preparation of α,β-unsaturated aldehydes [3, 4], 2-alkoxyvinyl ketones [5], heterocyclic compounds [6, 7], naphthalene derivatives [8], etc. However, the use of β-keto acetals is limited by their relatively low stability, which is manifested even toward agents of a basic character. With the object of obtaining compounds of this type that are more convenient for further applications, we undertook the synthesis of the corresponding cyclic acetals (1,3-dioxolane derivatives). As is well known, cyclic acetals are much more stable than open-chain acetals.

We prepared cyclic β-keto acetals [2-(2-oxoalkyl)-1,3-dioxolanes] by reaction of the corresponding 2-chlorovinyl ketones with ethylene glycol in an alkaline medium:



$$R-COCH=CHCl + HOCH_2CH_2OH \rightarrow RCOCH_2CH(OCH_2)_2$$

$R = CH_3,\ C_2H_5,\ C_3H_7;\ i\text{-}C_4H_9,\ C_5H_{11}.$

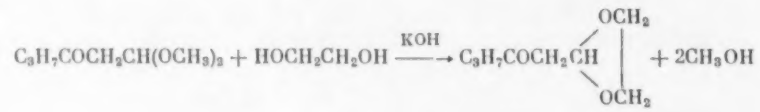
Taking the preparation of the first member of the series as an example, we investigated the reaction in detail with variation of the reaction conditions (in presence of potassium hydroxide, potassium carbonate, sodium hydroxide, sodium carbonate, sodium bicarbonate). The best results were obtained when potassium carbonate or potassium hydroxide was used as the alkaline reagent, use of the latter being preferable for the preparation of the higher homologs since reaction was then more rapid and gave better yields. The cyclic β-keto acetals were obtained in 50-65% yields.

We applied this method also to the synthesis of β-keto acetals containing an aryl radical, using for this purpose aryl 2-chlorovinyl ketones, which have become readily accessible [9]. The literature [10] reports a synthesis of benzoylacetaldehyde diethyl acetal from 2-chlorovinyl phenyl ketone (3-chloroacrylophenone) and alcohol, but we encountered great difficulty in reproducing this synthesis in our laboratory and were able to obtain this acetal only in low yield and not altogether pure. In view of this, the preparation of cyclic β-keto acetals of the aromatic series is of special interest. Taking the preparation of the cyclic acetal of benzoylacetaldehyde as our example, we demonstrated the complete applicability of our method to the aromatic series. The yield of the cyclic acetal of benzoylacetaldehyde was 85%.

$$C_6H_5COCH=CHCl + HOCH_2CH_2OH \rightarrow C_6H_5COCH_2CH(OCH_2)_2$$

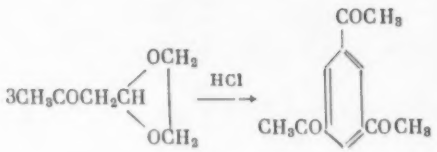
The previously unknown cyclic acetals of β-keto aldehydes which we obtained are colorless liquids of characteristic odor; they can be preserved for a long time unchanged. The acetal of benzoylacetaldehyde is a solid.

Our experiments showed that the cyclic acetals can be prepared also from open-chain acetals by heating the latter with ethylene glycol in presence of traces of alkali:

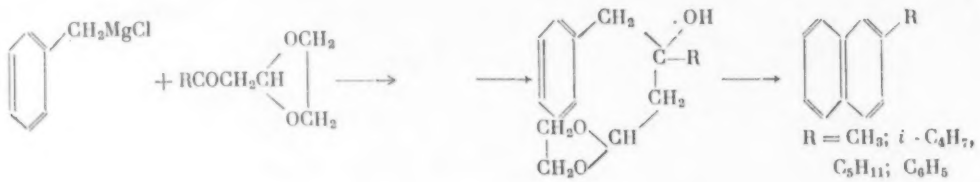


This peculiar reaction of "transacetaliziation" is very interesting in that it points directly to the higher stability of cyclic acetals, as compared with their open-chain analogs. For the simple cyclic keto acetals described in paper, this reaction is of no preparative value, but in other cases it may be useful from this point of view.

In principle, the chemical behavior of the cyclic acetals that we have prepared does not differ from that of their open-chain analogs [2, 3]. For example, hydrolysis of the cyclic acetal of acetoacetaldehyde with 10% hydrochloric acid gives 1,3,5-triacetylbenzene, which proves the structure of the compounds that we obtained:



In view of the high stability of the cyclic acetals, we applied them in the synthesis of alkylnaphthalenes by the method that we developed recently [8]:



As we expected, the yields of alkylnaphthalenes were considerably higher than those obtained by the use of open-chain acetals. The probable explanation is that, owing to the higher stability of the cyclic acetals, the first stage of the synthesis (reaction with the Grignard reagent) is not complicated by the side reaction of decomposition of the acetal, and formation of the tertiary alcohol is therefore more complete. In a similar way we prepared 2-phenylnaphthalene in 55% yield (on the amount of acetal taken). It should be noted that this compound has been very inaccessible until recently. Even in the most recent method of Campbell and Kidd [11], 2-phenylnaphthalene is obtained – again from benzyl chloride – by a complex eight stage synthesis in very low overall yield.

The suggested modification of the new synthesis of naphthalenes that we proposed recently [8] makes this method still more convenient and ensures quite satisfactory yields of alkylnaphthalenes. There is no doubt that further investigation of cyclic acetals will make it possible to apply it with success in other directions.

EXPERIMENTAL

Cyclic Acetal of Acetoacetaldehyde (2-Acetonyl-1,3-dioxolane)

A. A mixture of 78 g of finely ground potassium carbonate and 88 g of ethylene glycol was prepared in

a beaker provided with a stirrer. The suspension was stirred vigorously and cooled with ice and salt while 50 g of 4-chloro-3-buten-2-one was added over a period of 1.5-2 hours. Cooling was then discontinued, 30 ml of water was added, and the mixture was stirred further for 3-4 days. The precipitate was filtered off and washed with water and ether. The aqueous layer was extracted repeatedly with ether, and the combined ether extracts were dried over calcium chloride, the drying agent being changed several times. Ether was distilled off, and vacuum distillation of the residue gave a fraction of b.p. 81-83° (9 mm) in 51% yield (31.4 g).

B. A mixture of 65 ml of ethylene glycol and 20 g of potassium hydroxide was prepared in a flask fitted with stirrer and dropping funnel. The mixture was stirred vigorously and cooled with ice and salt while 37 g of 4-chloro-3-buten-2-one was added over a period of one hour. Cooling was then discontinued, and the mixture was stirred further for several days. The mixture was diluted with 80 ml of water and extracted repeatedly with ether. The extracts were dried over calcium chloride, ether was distilled off, and vacuum distillation of the residue gave a fraction of b.p. 81-83° (9 mm) in 47% yield (21.7 g).

After being redistilled the substance had b.p. 82-83° (9 mm); n_D^{20} 1.4400; d_4^{20} 1.1084; found MR 31.00; calculated MR 30.92.

Found %: C 55.11, 55.04; H 7.76, 7.82. $C_6H_{10}O_3$. Calculated %: C 55.37; H 7.75.

This acetal is a colorless oil, miscible with water and organic solvents. When carefully purified it can be kept for a long time without change. With aqueous ferric chloride it gives an intense red-brown color, which becomes still more intense with time.

Cyclic Acetal of 3-Oxovaleraldehyde [2-(2-Oxobutyl)-1,3-Dioxolane]

Reaction between 29.5 g of 1-chloro-1-penten-3-one, 55 ml of ethylene glycol, and 14 g of potassium hydroxide was carried out similarly (see above). Distillation gave a fraction of b.p. 90-92° (10 mm). After redistillation: b.p. 90-91° (10 mm); n_D^{20} 1.4420; d_4^{20} 1.0741; found MR 35.62; calculated MR 35.51; Yield 17.5 g (51 %).

Found %: C 58.19, 58.09; H 8.50, 8.43. $C_7H_{12}O_3$. Calculated %: C 58.32; H 8.39.

2-(2-Oxobutyl-1,3-dioxolane is a colorless oil, miscible with organic solvents, but sparingly soluble in water. It is stable to keeping.

Cyclic Acetal of 3-Oxohexanal [2-(2-Oxopentyl)-1,3-Dioxolane]

Reaction was carried out as described above between 40 g of 1-chloro-1-hexen-3-one, 70 ml of ethylene glycol, and 17 g of potassium hydroxide. Distillation gave a fraction of b.p. 92-94° (7-8 mm) in 56% yield (26.6 g). After being redistilled the substance had b.p. 92-93° (7 mm); n_D^{20} 1.4427; d_4^{20} 1.0440; found MR 40.14; calculated MR 40.24.

Found %: C 60.85, 60.79; H 9.03, 8.94. $C_8H_{14}O_3$. Calculated %: C 60.74; H 8.92.

The cyclic acetal of 3-oxohexanal is a colorless oil, miscible with organic solvents but insoluble in water. It is stable to keeping.

Cyclic Acetal of 5-Methyl-3-Oxohexanal [2-(4-Methyl-2-Oxopentyl)-1,3-Dioxolane]

Reaction was carried out as described above between 30 g of 1-chloro-5-methyl-1-hexen-3-one, 55 ml of ethylene glycol, and 12.2 g of potassium hydroxide. Distillation gave a fraction of b.p. 92-95° (6 mm) in 60% yield (21 g). After being redistilled the substance had b.p. 92-93° (4.5 mm); n_D^{20} 1.4429; d_4^{20} 1.0181; found MR 44.82; calculated MR 44.86.

Found %: C 62.51, 62.60; H 9.36, 9.37. $C_9H_{16}O_3$. Calculated %: C 62.77; H 9.37.

The 5-methyl-3-oxohexanal acetal is a colorless oil, miscible with organic solvents but insoluble in water. It is stable to keeping.

Cyclic Acetal of 3-Oxooctanal [2-(2-Oxoheptyl)-1,3-Dioxolane]

Reaction was carried out as described above between 40 g of 1-chloro-1-octen-3-one, 60 ml of ethylene glycol, and 15 g of potassium hydroxide. Distillation gave a fraction of b.p. 118-120° (8-9 mm) in 65% yield (30 g). After being redistilled the substance had b.p. 112-115° (6 mm); n_D^{20} 1.4471; d_4^{20} 1.0062; found MR 49.48; calculated MR 49.48.

Found %: C 64.18, 64.21; H 9.75, 9.78. $C_{10}H_{18}O_3$. Calculated %: C 64.48; H 9.74.

The 3-oxooctanal acetal is a colorless oil, miscible with organic solvents but insoluble in water. It is stable to keeping.

Cyclic Acetal of Benzoylacetaldehyde (2-Phenacyl-1,3-Dioxolane)

3-Chloroacrylophenone (25 g) was added slowly to a vigorously stirred cooled (ice and salt) solution of 9 g potassium hydroxide in 100 ml of ethylene glycol; the mixture was then stirred at room temperature for several days. The precipitate was filtered off, carefully washed with water, dried in a desiccator, and recrystallized from petroleum ether. More of the acetal was obtained by extraction of the mother liquor with ether and removal of the ether. Total yield 29 g (85%).

The substance forms yellowish needles, m.p. 58-59°.

Found %: C 69.37, 69.28; H 5.39, 5.44. $C_{11}H_{12}O_3$. Calculated %: C 69.45; H 5.31.

The benzoylacetaldehyde acetal is readily soluble in benzene and alcohol, but not so soluble in diethyl ether and petroleum ether. It is stable to keeping.

Hydrolysis of the Cyclic Acetal of Acetoacetaldehyde

The acetal (1.1 g) was mixed with 10 ml of 10% hydrochloric acid and left overnight. The precipitate was filtered off and recrystallized from acetic acid; yield 0.3 g; m.p. 162-163°, undepressed by admixture with known triacetylbenzene. For triacetylbenzene the literature gives m.p. 163° [12], m.p. 162-162.5° [2].

Reaction of 3-Oxohexanal Dimethyl Acetal with Ethylene Glycol

A mixture of 10 g of 3-oxohexanal dimethyl acetal and 4.5 g of ethylene glycol was refluxed in presence of a small piece of potassium hydroxide for two hours. The reflux condenser was then replaced by one set for distillation, and methanol was distilled off (b.p. 64-65°; n_D^{20} 1.3302). Vacuum distillation of the residue gave 8.5 g (86%) of the cyclic acetal of 3-oxohexanal, b.p. 92-94° (7 mm) and n_D^{20} 1.4431.

2-Methylnaphthalene

A solution of 13.2 g of the cyclic acetal of acetoacetaldehyde in 20 ml of ether was added to a stirred cooled solution of benzylmagnesium chloride prepared in the usual way from 16.7 g of benzyl chloride and 3.7 g of magnesium in 70 ml of ether. The usual treatment (decomposition with ammonium chloride solution) gave the tertiary alcohol, which was cyclized without being purified; the alcohol was added to 230 ml of boiling glacial acetic acid, and to the resulting solution 110 ml of 42% hydrobromic acid was added in one portion. The reaction mixture was heated to the boil for 3-4 minutes, cooled, diluted with water, neutralized with alkali, and extracted with ether. The extract was dried over magnesium sulfate, ether was distilled off, and the residue was vacuum-distilled. A fraction was collected which boiled at 100-102° (9 mm); it solidified in the receiver; yield 4.0 g (28%). Recrystallization from petroleum ether gave colorless crystals of m.p. 34-35°, undepressed by admixture of known 2-methylnaphthalene. The literature gives m.p. 35-36°, b.p. 100-102° (9 mm) [8]; m.p. 34.3°, b.p. 241° [13].

The picrate was prepared in alcohol and recrystallized from the same solvent; yellow needles; m.p. 116-117°. The literature gives m.p. 116-117° [8], m.p. 116-117° [14].

2-Isobutylnaphthalene

2-Isobutylnaphthalene was prepared similarly from 12.9 g of benzyl chloride, 2.5 g of magnesium, and 12.8 g of the cyclic acetal of 5-methyl-3-oxohexanal. The resulting alcohol was cyclized by the action of a

mixture of 180 ml of glacial acetic acid and 90 ml of 42% hydrobromic acid. Two vacuum distillations gave a fraction of b.p. 113-115°; yield 5.6 g (40.5% on the amount of acetal taken). After being redistilled the substance had b.p. 114-114.5° (5 mm); n_D^{20} 1.5732; d_4^{20} 0.9605.

Found %: C 90.81, 90.83; H 8.77, 8.82. $C_{14}H_{16}$. Calculated %: C 91.24; H 8.75.

2-Isobutylnaphthalene is a colorless oil of feeble odor, miscible with organic solvents, insoluble in water. The literature gives b.p. 112-113° (6 mm) [15].

2-Pentylnaphthalene

2-Pentylnaphthalene was prepared similarly from 12 g of benzyl chloride, 2.3 g magnesium, and 12.8 g of the cyclic acetal of 3-oxooctanal. The resulting alcohol was cyclized by the action of a mixture of 150 ml of glacial acetic acid and 80 ml of 42% hydrobromic acid. Two vacuum distillations gave a fraction of b.p. 143-145° (8 mm) in a yield of 5.95 g (45% on the amount of acetal taken). After being redistilled the substance had b.p. 144-145° (8 mm); n_D^{20} 1.5663; d_4^{20} 0.9564. The literature gives b.p. 143-145° (8 mm); n_D^{20} 1.5663; d_4^{20} 0.9562 [8]; b.p. 310°; n_D^{20} 1.5694; d_4^{20} 0.956 [16].

The crystallization compound with trinitrobenzene formed yellow needles, m.p. 75°, undepressed in admixture with a known sample. The literature gives m.p. 75° [8], m.p. 74° [14].

2-Phenylnaphthalene

A solution of 12.6 g of the cyclic acetal in 120 ml of ether was added to a solution of benzylmagnesium chloride prepared from 9.5 g of benzyl chloride, 1.8 g of magnesium, and 40 ml of ether. The mixture was stirred for two hours at room temperature and for one hour at the boil. Decomposition with ammonium chloride solution and the usual treatment gave the tertiary alcohol, which, without being purified, was cyclized as described above by the action of a mixture of 160 ml of glacial acetic acid and 90 ml of 42% of hydrobromic acid. The reaction mixture was diluted with water and neutralized with alkali. The precipitate was filtered off, washed with water, and recrystallized from alcohol. The yield of 2-phenylnaphthalene was 7.4 g (55% on the amount of the acetal taken); colorless crystals, m.p. 101-101.5°.

Found %: C 94.17, 94.16; H 6.12, 6.05. $C_{16}H_{12}$. Calculated %: C 94.08; H 5.92.

The literature gives m.p. 101-102° [11]. The crystallization compound with trinitrobenzene had m.p. 112-113°; the literature gives m.p. 112-113° [11].

SUMMARY

1. A general method was developed for the synthesis of cyclic acetals of β-keto aldehydes by reaction of β-chlorovinyl ketones with ethylene glycol in presence of alkaline agents. Yields of 50-85% were obtained.

2. It was shown that heating of open-chain β-keto acetals with ethylene glycol in presence of alkali results in transacetalization with formation of the corresponding cyclic acetals.

3. It was shown that the use of cyclic acetals for the synthesis of alkylnaphthalenes by the method that we developed previously [8] makes it possible to obtain these naphthalenes in higher yield.

LITERATURE CITED

[1] O. Nelles, US Patent, 2091373; C. A. 31, 744 (1937).

[2] A. N. Nesmeyanov, N. K. Kochetkov, and M. I. Rybinskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1951, 395.

[3] C. Price, and J. Pappalardo, J. Am. Chem. Soc. 72, 2613 (1950).

[4] E. Royals, and K. Brannock, J. Am. Chem. Soc. 76, 1180 (1954).

[5] E. Royals, and K. Brannock, J. Am. Chem. Soc. 76, 3041 (1954).

[6] N. K. Kochetkov, Proc. Acad. Sci. USSR 84, 741 (1952).

[7] W. Franke, and R. Kraft, Ber. 86, 797 (1953).

[8] N. K. Kochetkov, E. E. Nifantyev, and A. N. Nesmeyanov, Proc. Acad. Sci. USSR 104, 422 (1955).*

[9] N. K. Kochetkov, A. Ya. Khorlin, and M. Ya. Karpeisky, J. Gen. Chem. 26, 595 (1956).*

[10] L. Panizzi, Gazz. 77, 549 (1948).

[11] N. Campbell, and D. Kidd, J. Chem. Soc. 1954, 2154.

[12] L. Claisen, and N. Stylos, Ber. 21, 1145 (1888).

[13] S. Morell, G. Pickering, and J. Smith, J. Inst. Petrol. 34, 677 (1948).

[14] Yu. G. Mamedaliev and Sh. T. Akhmetov, Prog. Chem. 23, 876 (1954).

[15] G. Darzens, and H. Rost, Compt. rend. 146, 934 (1908).

[16] A. Bailey, G. Pickering, and J. Smith, J. Inst. Petrol. 35, 103 (1949).

M. V. Lomonosov State University
Moscow

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SYNTHESIS OF α,α,α,ω,ω,ω-HEXAMETHYLPOLY(ETHYLVINYLSILOXANES)

K. A. Andrianov and N. A. Kurasheva

Linear α,α,α,ω,ω,ω-hexamethylpoly(dimethylsiloxanes) have been described in the literature and their properties have been studied. It would be of interest also to synthesize linear polyorganosiloxanes containing silicon-attached vinyl groups. In the present investigation we prepared α,α,α,ω,ω,ω-hexamethylpoly(ethylvinylsiloxanes) by the cohydrolysis of dichloroethylvinylsilane and chlorotrimethylsilane. Experiments showed that, when a mixture of dichloroethylvinylsilane and chlorotrimethylsilane was added to water, reaction proceeded as follows:

$$x\,CH_2=CHSiCl_2(C_2H_5) + 2(CH_3)_3SiCl + (x+2)\,H_2O \longrightarrow$$

$$\longrightarrow (CH_3)_3Si-O\left[-Si(C_2H_5)(CH=CH_2)-O\right]_x-Si(CH_3)_3 + (2x+2)\,HCl$$

By variation of the molar ratio of dichloroethylvinylsilane to chlorotrimethylsilane, we prepared and isolated α,α,α,ω,ω,ω-hexamethylpoly(ethylvinylsiloxanes) for which x = 1, 2, 3, and 4. It should be noted that, irrespective of the proportion of dichloroethylvinylsilane taken, the main product – a hexamethylpoly(ethylvinylsiloxane) of given degree of polymerization – was always accompanied by polymers of higher and lower degrees of polymerization.

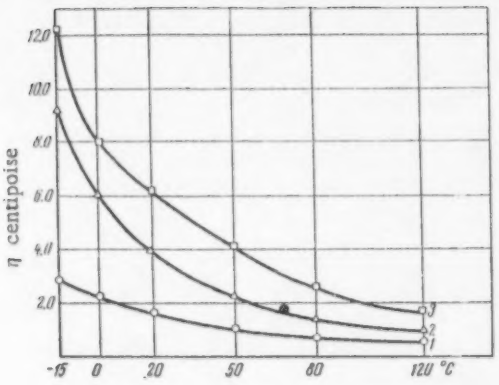
All the linear α,α,α,ω,ω,ω-hexamethylpoly(ethylvinylsiloxanes) obtained (x = 1-4) are stable liquids at room temperature; they can be vacuum-distilled without decomposition. Investigation of the viscosity of α,α,α,ω,ω,ω-hexamethylpoly(ethylvinylsiloxanes) showed that their viscosities• in the temperature range from – 15° to [120° (see Figure) are 4.9 for 3-ethyl-1,1,15,5,5-hexamethyl-3-vinyltrisiloxane, 9.7 for 3,5-diethyl-1,1,1,7,7,7-hexamethyl-3,5-divinyltetrasiloxane, and 11.8 for 3,5,7-triethyl-1,1,1,9,9,9-hexamethyl-3,5,7-trivinylpentasiloxane. These values are close to those for linear poly(dimethylsiloxanes). The activation energy for viscous flow in the same temperature range is 2539 cal for 3-ethyl-1,1,1,5,5,5-hexamethyl-3-vinyltrisiloxane, 3224 cal for 3,5-diethyl-1,1,1,7,7,7-hexamethyl-3,5-divinyltetrasiloxane, and 3532 cal for 3,5,7-triethyl-1,1,1,9,9,9-hexamethyl-3,5,7-trivinylpentasiloxane. These values are somewhat higher than those for linear poly(dimethylsiloxanes): for decamethyltetrasiloxane the activation energy is 2510 cal [1].

By the cohydrolysis of trichlorovinylsilane and chlorotrimethylsilane we obtained tris(trimethylsiloxy)-vinylsilane:

$$CH_2=CHSiCl_3 + 3(CH_3)_3SiCl + 3H_2O \rightarrow CH_2=CHSi[OSi(CH_3)_3]_3 + 6HCl.$$

The properties of the new compounds obtained are given in Table 1. Table 2 gives the properties of new derivatives of dichloroethylvinylsilane.

• The translation "viscosities" is correct, although the "viscosities" cited do not correspond to any given temperature in the range stated (see Figure). – Publisher.



Temperature-dependence of viscosity: 1) 3-ethyl-1,1,1,5,5,5-hexamethyl-3-vinyltrisiloxane; 2) 3,5-diethyl-1,1,1,7,7,7-hexamethyl-3,5-divinyltetrasiloxane; 3) 3,5,7-triethyl-1,1,1,9,9,9-hexamethyl-3,5,7-trivinylpentasiloxane.

EXPERIMENTAL

Preparation of Dichloroethylvinylsilane

Magnesium (24 g), previously treated with ether, was placed in a three-necked flask fitted with stirrer, reflux condenser, and thermometer, and ether (200 ml) was added. A solution of 109 g of ethyl bromide in 100 ml of ether was added from a dropping funnel. When reaction set in, as indicated by evolution of heat, the stirrer was switched on. Reaction proceeded at 34-38° until the magnesium turnings disappeared (5-6 hours). The resulting Grignard reagent was transferred to another flask, and a solution of 166 g of trichlorovinylsilane in 100 ml of ether was placed in the three-necked flask. The solution was stirred while the Grignard reagent was added, when reaction proceeded for a period of seven hours with evolution of heat (35-38°) and formation of a white precipitate. The whole mixture was then transferred to a Wurtz flask, and the liquid was distilled from the precipitate on an oil bath. The liquid was fractionated through a 10-plate column. Dichloroethylvinylsilane came over at 127-128° in a yield of 44.82 g (28.91%); d_4^{20} 1.0416; n_D^{20} 1.4302; found MR 38.12; calculated MR 38.69. The literature [2] gives b.p. 125°.

Found %: C 31.62; H 6.05; Si 12.43; Cl 44.39. $C_4H_8SiCl_2$. Calculated %: C 30.96; H 5.16; Si 11.61; Cl 45.80.

Cohydrolysis of Dichloroethylvinylsilane and Chlorotrimethylsilane

a) Synthesis of 3-ethyl-1,1,1,5,5,5-hexamethyl-3-vinyltrisiloxane. With mechanical stirring, a mixture of 15.5 g (0.1 mole) of dichloroethylvinylsilane and 21.72 g (0.2 mole) of chlorotrimethylsilane was added to 130 ml of distilled water in a water-cooled flask over a period of one hour; the reaction temperature was 28-30°. When the addition was complete, the oily layer of reaction product was separated from the aqueous layer and washed with water until reaction for chloride was negative. The yield of oil was 24.0 g (91.6%), and the fraction isolated, amounting to 7.8 g (29.77%), had b.p. 45-48° (5 mm); d_4^{20} 0.8421; n_D^{20} 1.4011; found M 267.3; calculated M 262; found MR 76.38; calculated MR 76.39.

Found %: C 44.62; H 10.45; Si 30.08. $C_{10}H_{26}O_2Si_3$. Calculated %: C 45.80; H 9.92; Si 32.05.

b) Synthesis of 3,5-diethyl-1,1,1,7,7,7-hexamethyl-3,5-divinyltetrasiloxane. The synthesis of the diethylhexamethyldivinyltetrasiloxane was carried out similarly. From 22 g (0.142 mole) of dichloroethylvinylsilane and 18.21 g (0.168 mole) of chlorotrimethylsilane we obtained 26.2 g of oil (86.29%). Vacuum fractionation of the oil gave a fraction of b.p. 98-110° (5 mm), amounting to 5.5 g (20.99%); it had d_4^{20} 0.8982; n_D^{20} 1.4157; found M 361; calculated M 362; found MR 102.99; calculated MR 103.89.

Found %: C 45.12; H 9.73; Si 28.96. $C_{14}H_{34}O_3Si_4$. Calculated %: C 46.40; H 9.39; Si 30.93.

c) Synthesis of 3,5,7-tiethyl-1,1,1,9,9,9-hexamethyl-3,5,7-trivinylpentasiloxane. The synthesis of the triethylhexamethyltrivinylpentasiloxane was carried out similarly. From 30.62 g (0.198 mole) of dichloroethylvinylsilane and 14.32 g (0.131 mole) of chlorotrimethylsilane we obtained 16.8 g (55.17%) of oil. Vacuum fractionation of the oil gave 7.6 g (24.95%) of a fraction of b.p. 145-152° (5 mm); n_D^{26} 1.4215; d_4^{26} 0.9235; found MR 128.95; calculated MR 130.4.

Found %: C 45.69; H 9.84; Si 28.81. $C_{18}H_{24}O_4Si_5$. Calculated %: C 46.75; H 9.09; Si 30.30.

TABLE 1

Name of substance	Chemical formula	B. p. in °C (p in mm)	n_D^{20}	d_4^{20}	*MR* found	*MR* calculated
3-Ethyl-1,1,1,5,5,5-hexamethyl-3-vinyltrisiloxane	$(CH_3)_3Si-O\left[\begin{array}{c}C_2H_5\\ \vert\\ -Si-O\\ \vert\\ CH=CH_2\end{array}\right]_1-Si(CH_3)_3$	45—48 (5)	1.4011	0.8421	76.38	76.39
3,5-Diethyl-1,1,1,7,7,7-hexamethyl-3,5-divinyltetrasiloxane	$(CH_3)_3Si-O\left[\begin{array}{c}C_2H_5\\ \vert\\ -Si-O\\ \vert\\ CH=CH_2\end{array}\right]_2-Si(CH_3)_3$	98—110 (5)	1.4157	0.8982	102.99	103.89
3,5,7-Triethyl-1,1,1,9,9,9-hexamethyl-3,5,7-trivinylpentasiloxane	$(CH_3)_3Si-O\left[\begin{array}{c}C_2H_5\\ \vert\\ -Si-O\\ \vert\\ CH=CH_2\end{array}\right]_3-Si(CH_3)_3$	145—152 (5)	1.4215	0.9235	128.95	130.4
3,5,7,9-Tetraethyl-1,1,1,11,11,11-hexamethyl-2,5,7,9-tetravinylhexasiloxane	$(CH_3)_3Si-O\left[\begin{array}{c}C_2H_5\\ \vert\\ -Si-O\\ \vert\\ CH=CH_2\end{array}\right]_4-Si(CH_3)_3$	171—190 (5)	1.4284	0.9457	152.14	158.9
Tris(trimethylsiloxy)vinylsilane	$CH_2=CHSi[OSi(CH_3)_3]_3$	133—140 (4)	1.4099	0.9432	84.69	90.44

d) Synthesis of 3,5,7,9-tetraethyl-1,1,1,11,11,11-hexamethyl-3,5,7,9-tetravinylhexasiloxane. The synthesis of the tetraethylhexamethyltetravinylhexasiloxane was carried out similarly. From 31.63 g (0.204 mole) of dichloroethylvinylsilane and 11.1 g (0.10 mole) of chlorotrimethylsilane we obtained 25.6 g (89.28%) of oil. Vacuum fractionation of the oil gave 2.37 g (9.25%) of a fraction of b.p. 171-190° (5 mm); n_D^{20} 1.4284; d_4^{20} 0.9457; found M 546.2; calculated M 562; found MR 152.14; calculated MR 158.9.

Found %: C 44.71; H 9.36; Si 28.36. $C_{22}H_{50}O_5Si_6$. Calculated C 46.97; H 8.89; Si 29.89.

e) Synthesis of tris(trimethylsiloxy)vinylsilane. Distilled water (400 ml) was placed in a three-necked flask fitted with stirrer, reflux condenser, and thermometer. The water was heated to 80° and stirred vigorously while addition was made over a period of 2.5 hours of a mixture of 40.4 g (0.25 mole) of trichlorovinylsilane and 81.5 g (0.75 mole) of chlorotrimethylsilane (temperature 80-86°). When the addition was complete, the mixture was stirred for 30 minutes, cooled, and transferred to a separating funnel, in which it was washed until reaction for chloride was negative. The oil was dried, and vacuum distillation gave 14.08 g (4.4%) of a fraction of b.p. 133-140° (4 mm); n_D^{20} 1.4099; d_4^{20} 0.9432; found MR 84.69; calculated MR 90.44.

Found %: C 39.45; H 8.7; Si 34.27. $C_{11}H_{30}O_3Si_4$. Calculated %: C 40.99; H 9.32; Si 34.78.

TABLE 2

Name of substance	Chemical formula	B. p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR found	MR calculated
Dichloroethylvinylsilane	$CH_2=CHSiCl_2$ | C_2H_5	127—128	1.4302	1.0416	38.69	38.12
Diethoxyethylvinylsilane	$CH_2=CHSi(OC_2H_5)_2$ | C_2H_5	149—152	1.4062	0.8850	48.97	49.88
Diacetoxyethylvinylsilane	$CH_2=CHSi(OCOCH_3)_2$ | C_2H_5	54—56 (4)	1.4165	1.0216	49.66	49.93
Dibutoxyethylvinylsilane	$CH_2=CHSi(OC_4H_9)_2$ | C_2H_5	71—78 (5)	1.4146	0.8509	67.63	68.47
Ethyldiisobutoxyvinylsilane	$CH_2=CHSi(i\text{-}OC_4H_9)_2$ | C_2H_5	60—61 (4)	1.4139	0.8494	67.75	68.47

Synthesis of Diethoxyethylvinylsilane

An excess of absolute ethanol (12 g, i.e., 0.26 mole) was added with stirring to 18.42 g (0.11 mole) of dichloroethylvinylsilane contained in a three-necked flask fitted with reflux condenser, thermometer, and stirrer. At first the temperature of the reaction mixture fell to 16°. After addition of all the alcohol the mixture was heated at 65-70° until hydrogen chloride ceased to be evolved (19 hours). The product was transferred to a flask fitted with a Vigreux column and distilled. A yield of 6.25 g (30.2%) of diethoxyethylvinylsilane was obtained; b.p. 149-152°; n_D^{20} 1.4062; d_4^{20} 0.8850; found MR 48.97; calculated MR 49.88.

Found %: Si 15.68. $C_8H_{18}O_2Si$. Calculated %: Si 16.09.

Synthesis of Dibutoxyethylvinylsilane

This was synthesized similarly from 15.57 g (0.1 mole) of dichloroethylvinylsilane and 15.02 g (0.2 mole) of butyl alcohol at 70-80°. Vacuum fractionation gave 5.6 g (24.3%) of a substance having d_4^{20} 0.8509; n_D^{20} 1.4146; found MR 67.63; calculated MR 68.47.

Found %: C 60.04; H 11.61; Si 11.80. $C_{12}H_{26}O_2Si$. Calculated %: C 62.60; H 11.30; Si 12.17.

Synthesis of Ethyldiisobutoxyvinylsilane

Ethyldiisobutoxyvinylsilane was prepared similarly from 12 g (0.077 mole) of dichloroethylvinylsilane and 14 g (0.19 mole) of isobutyl alcohol. The product, amounting to 8.1 g (45.7%), had b.p. 60-61° (4 mm); d_4^{20} 0.8479; n_D^{20} 1.4139; found MR 67.75; calculated MR 68.47.

Found %: C 60.58; H 10.60; Si 12.00. $C_{12}H_{26}O_2Si$. Calculated %: C 62.20; H 11.30; Si 12.17.

Synthesis of Diacetoxyethylvinylsilane

Toluene (25 ml) was added to 11.0 g (0.13 mole) of anhydrous sodium acetate contained in a three-necked flask fitted with reflux condenser, stirrer, and thermometer. The stirrer was switched on, and 10.4 g (0.065 mole) of dichloroethylvinylsilane was added. The temperature of the reaction mixture gradually rose to 70-80°. The mixture was heated for 17 hours. Common salt was then removed by filtration through a Buchner funnel. Vacuum fractionation of the liquid gave 5.8 g (42.8%) of a liquid having b.p. 54-56° (4 mm); d_4^{20} 1.0216; n_D^{20} 1.4165; found MR 49.66; calculated MR 49.93; ($OCOCH_3$) 58.41%; (theoretical: 58.42%).

Found %: C 48.30; H 6.73; Si 13.49. $C_8H_{14}O_4Si$. Calculated %: C 47.52; H 6.93; Si 13.31.

SUMMARY

1. Linear α,α,α,ω,ω,ω-hexamethylpoly(ethylvinylsiloxanes) were synthesized by cohydrolysis of dichloroethylvinylsilane and chlorotrimethylsilane, and their viscosities were studied in the temperature range from -15° to +120°. It was found that their viscosities were close in value to those of linear poly(dimethylsiloxanes) and that their activation energies for viscous flow were somewhat higher than those of linear poly(dimethylsiloxanes).

2. Derivatives of dichloroethylvinylsilane were prepared, and their properties were studied.

LITERATURE CITED

[1] M. J. Hunter, E. L. Warrick, J. E. J. Hyde, and C. C. Currie, J. Am. Chem. Soc. 68, 2284 (1946).

[2] Geo. H. Wagner, US Patent 2637738 (5. V. 1953); Chem. Abst. 48, 14 (1954).

Institute of Heteroorganic Compounds of
the Academy of Sciences of the USSR

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STABILITY OF THE SILICON-CARBON BOND IN ar-CHLORINATED TRICHLOROPHENYL – AND DICHLOROETHYLPHENYL-SILANES

K. A. Andrianov and V. A. Odinets

The stability of the silicon-carbon bond toward various reagents is of considerable interest. Various investigations have been devoted to the scission of tetrasubstituted silanes including chloroalkylsilanes. It is known from the literature that treatment of trimethylphenylsilane and its derivatives with hydrogen chloride in glacial acetic acid causes the phenyl group to split off. It was shown that phenyl is more readily split off than the p- and m-chlorophenyl groups [1]. The results on the scission of (chlorophenyl)trimethylsilanes indicate that the chlorine atom in these compounds has a deactivating effect. Studies of the scission of tetrasubstituted alkyl(aryl)silanes with hydrogen chloride in a medium of glacial acetic acid and concentrated sulfuric acid showed that scission is facilitated when the tetrasubstituted silanes have substituents capable of driving electrons into the Si-C bond [2, 3]. The scission of the Si-C bond with alkalis, amides, and alkoxides has also been studied. It was shown that tetraalkylsilanes are stable in an alkaline medium, but aliphatic tetrasubstituted silanes containing halogen in the substituents can undergo scission with rupture of an Si-C bond [4-7].

Rupture of an Si-C bond is facilitated by increase in the number of halogen atoms in the alkyl groups. Unsaturated organic radicals are more readily split off than saturated. Tetrasubstituted silanes containing a phenyl group are the least stable [8, 9]. Methyl and chloromethyl groups attached to silicon in chloromethylsilanes are split off by alkalis, the readiness with which ruputure takes place increasing as the extent to which hydrogen of the methyl group is replaced by halogen. As will be seen from the review of the literature, investigations on the stability of the Si-C bond have been carried out only with tetrasubstituted alkylarylsilanes and chloromethylsilanes. It would undoubtedly be of great interest to determine the stability of the Si-C bond in the hydrolysis of compounds containing chlorine in the aromatic nucleus, in particular of dichloro(chlorophenyl)ethylsilanes and trichloro(chlorophenyl)silanes. Our experiments showed that hydrolysis of trichloro(chlorophenyl)silanes at 38-40°, irrespective of the positions and number of chlorines in the phenyl groups, both in acid and in alkaline media, proceeds without appreciable rupture of Si-C bonds in accordance with the equation:

$$x\mathrm{Cl}_n\mathrm{C}_6\mathrm{H}_{5-n}\mathrm{SiCl}_3 \xrightarrow{3x\,\mathrm{H_2O}} (\mathrm{Cl}_n\mathrm{C}_6\mathrm{H}_{5-n}\mathrm{SiO}_{1,5})_x + 3x\mathrm{HCl}.$$

No appreciable variation was found in the stabilities of the bonds between silicon and carbon of the phenyl group in trichloro(chlorophenyl)silanes containing ar-chlorine in the 4-, 2,4-, 2,4,6-, 2,3,4,6-, and 2,3,4,5,6-positions.

Dichloro(chlorophenyl)ethylsilanes are also hydrolyzed in acid and alkaline media without elimination of chlorophenyl and ethyl groups:

$$x\begin{matrix}\mathrm{Cl}_n\mathrm{C}_6\mathrm{H}_{5-n}\\ \mathrm{C_2H_5}\end{matrix}\!\!>\!\mathrm{SiCl_2} \xrightarrow{2x\,\mathrm{H_2O}} \left(\begin{matrix}\mathrm{Cl}_n\mathrm{C}_6\mathrm{H}_{5-n}\\ \mathrm{C_2H_5}\end{matrix}\!\!>\!\mathrm{SiO}\right)_x + 2x\mathrm{HCl}.$$

These reaction equations are confirmed by the analysis of the polymers obtained.

The experimental results on the hydrolysis of trichloro(chlorophenyl)silanes and dichloro(chlorophenyl)-ethylsilanes in acid and alkaline media show that introduction of chlorine atoms in the phenyl group increases the polarity of the Si-C bond to a considerably less extent than the introduction of chlorine into a methyl group. Thus, the trichloromethyl group is split from the silicon atom by the action of water at room temperature, the dichloromethyl group split off at 45°, but the chloromethyl group is split off only at 110° under the action of a 10% solution of potassium hydroxide in butyl alcohol.

Treatment of trichloro(chlorophenyl)silanes at 38-40° with 10-16% aqueous caustic alkali and with 10-14% hydrochloric acid does not result in elimination of phenyl, chlorophenyl, dichlorophenyl, trichlorophenyl, tetrachlorophenyl, and pentachlorophenyl groups. Introduction of a nitro group into tetraphenylsilane greatly increases the electronegativity of the aromatic nucleus and the positive polarization of the silicon, and it greatly facilitates the elimination of a phenyl group in an alkaline medium. Scission of the Si-C bond is activated by the presence of methoxy and even methyl groups in the phenyl radical. Chlorine in trichloro(chlorophenyl)-silanes and dichloro(chlorophenyl)ethylsilanes deactivates the phenyl nucleus and scission of the Si-C bond is absent both in acid and in alkaline media. Increase in the number of chlorine atoms in the phenyl group from one to five in trichloro(chlorophenyl)silanes and from one to four in dichloro(chlorophenyl)ethylsilanes has no appreciable effect on the stability of the Si-C bond to the action of alkaline and acid media – as can be seen from the table.

Formula of original compound	General formula of hydrolysis product	C : Si			Cl : Si		
		calculated	found		calculated	found	
			acid medium	alkaline medium		acid medium	alkaline medium
$ClC_6H_4SiCl_3$	$(ClC_6H_4SiO1.5)_n$	2.57	2.68	2.27	1.26	1.32	1.15
$Cl_2C_6H_3SiCl_3$	$(Cl_2C_6H_3SiO1.5)_n$	2.57	2.66	2.08	2.53	2.32	—
$Cl_3C_6H_2SiCl_3$	$(Cl_3C_6H_2SiO1.5)_n$	2.57	2.61	2.04	—	—	—
$Cl_4C_6HSiCl_3$	$(Cl_4C_6HSiO1.5)_n$	2.57	2.63	2.23	—	—	—
$Cl_5C_6SiCl_3$	$(Cl_5C_6SiO1.5)_n$	2.57	2.65	2.31	6.32	6.45	5.49
$ClC_6H_4(C_2H_5)SiCl_2$	$\left(ClC_6H_4(C_2H_5)SiO\right)_n$	3.42	3.39	3.07	1.26	1.28	1.18
$Cl_2C_6H_3(C_2H_5)SiCl_2$	$\left(Cl_2C_6H_3(C_2H_5)SiO\right)_n$	3.42	3.39	3.27	2.53	2.65	2.46
$Cl_3C_6H_2(C_2H_5)SiCl_2$	$\left(Cl_3C_6H_2(C_2H_5)SiO\right)_n$	3.42	3.18	3.29	3.80	3.20	3.25
$Cl_4C_6H(C_2H_5)SiCl_2$	$\left(Cl_4C_6H(C_2H_5)SiO\right)_n$	3.42	3.5	3.30	—	—	—

EXPERIMENTAL

The trichloro(chlorophenyl)silanes used for hydrolysis were prepared by the chlorination of trichlorophenylsilane, and the dichloro(chlorophenyl)ethylsilanes were prepared from the corresponding trichloro(chlorophenyl)silanes and ethylmagnesium bromide.

A. Preparation of Trichloro(chlorophenyl)silanes [10]. A mixture of 211 g (1 mole) of trichlorophenylsilane (b.p. 201°, chlorine content 50.05%) and 1.05 g (0.5% on the weight of the silane) of anhydrous ferric chloride was prepared in a three-necked flask fitted with stirrer, thermometer, and reflux condenser. The reaction mixture was heated to 60°, and chlorine was passed into the flask at a rate of 0.1-0.2 liter/minute. The course of the chlorination was followed by observation of the change in density. The temperature was maintained at 70-80° and chlorination was continued for 10-15 hours. Vacuum fractionation of the chlorinated trichlorophenylsilane gave: trichloro(4-chlorophenyl)silane, b.p. 90-95° (10 mm) and d_4^{20} 1.4102; trichloro(2,4-dichlorophenyl)silane, b.p. 105-110° (10 mm) and d_4^{20} 1.4801; trichloro(2,4,6-trichlorophenyl)silane, b.p. 123-125° (10 mm) and d_4^{20} 1.5530.

As a result of further chlorination we isolated small amounts of trichloro(2,3,4,6-tetrachlorophenyl)silane, b.p. 135-137° (10 mm) and d_4^{20} 1.6210, and trichloro(2,3,4,5,6-pentachlorophenyl)silane, b.p. 147-150° (10 mm).

B. Preparation of dichloro(chlorophenyl)ethylsilanes. Magnesium turnings were moistened with ether and heated at 36.38° in a three-necked flask. As a reaction promotor, 20 g of a 1:5 mixture of ethyl bromide and ether was then added dropwise from a funnel. A mixture of the calculated amount of chlorinated trichlorophenylsilane, ethyl bromide, and toluene was then added slowly from the dropping funnel. The addition was made with vigorous stirring. The reaction temperature was maintained at 38-40°. When the addition was complete, the product was stirred further for two hours at 70-80° and then cooled and filtered. The filtrate was vacuum-distilled. The following dichloro(chlorophenyl)ethylsilanes, prepared by this method, were used for the hydrolysis: dichloro(4-chlorophenyl)ethylsilane, b.p. 116-118° (7 mm) and d_4^{20} 1.2947; dichloro(2,4-dichlorophenyl)ethylsilane, b.p. 130-132° (10 mm) and d_4^{20} 1.4381; dichloroethyl(2,4,6-trichlorophenyl)silane, b.p. 142-144° (12 mm) and d_4^{20} 1.4921; and dichloroethyl(2,3,4,6-tetrachlorophenyl)silane, b.p. 123-125° (3 mm) and d_4^{20} 1.5396.

I. Hydrolysis of Trichloro(chlorophenyl)silanes in an Acid Medium

a) Hydrolysis of trichloro(4-chlorophenyl)silane. A solution of 10 g (0.04 mole) of trichloro(4-chlorophenyl)silane in 20 ml of ether was added over a period of 3-5 minutes to a continuously stirred mixture of 30 g of water and 30 ml of ether in the reaction flask. When the addition was complete stirring was continued for 30 minutes. The reaction temperature was not allowed to exceed 40°. The organic layer was separated from the aqueous layer, washed with water, and dried. The solution was filtered, and ether was removed, first by distillation at atomspheric pressure and then by subjection to a vacuum (15 mm) at 40° until constant weight was attained. The resulting brittle polymer (6.3 g) was soluble in benzene, toluene, acetone, gasoline, and other organic solvents.

Found %: C 42.95, 42.73; H 2.96, 2.72; Si 16.23, 15.98; Cl 21.2, 21.4. $(ClC_6H_4SiO_{1.5})_n$. Calculated %: C 44.05; H 2.44; Si 17.13; Cl 21.68.

b) Hydrolysis of trichloro(2,4-dichlorophenyl)silane. Hydrolysis was carried out as above; 10 g (0.035 mole) of trichloro(2,4-dichlorophenyl)silane was taken. After removal of hydrochloric acid by washing and drying to constant weight, 6.5 g of brittle polymer was obtained.

Found %: C 36.82, 36.85; H 2.38, 2.49; Si 13.98, 13.62; Cl 32.5, 31.7. $(Cl_2C_6H_3SiO_{1.5})_n$. Calculated %: C 36.37; H 1.56; Si 14.15; Cl 35.85.

c) Hydrolysis of trichloro(2,4,6-trichlorophenyl)silane. The hydrolysis was carried out similarly; 10 g (0.031 mole) of trichloro(2,4,6-trichlorophenyl)silane was taken, and 6.2 g of polymer was obtained.

Found %: C 32.8, 33.5; H 1.89, 2.04; Si 13.19, 13.09. $(Cl_3C_6H_2SiO_{1.5})_n$. Calculated %: C 30.98; H 0.87; Si 12.05.

d) Hydrolysis of Trichloro(2,3,4,6-tetrachlorophenyl)silane. The hydrolysis was carried out similarly; 10 g (0.028 mole) of trichloro(2,3,4,6-tetrachlorophenyl)silane was taken, and 6.1 g of polymer was obtained.

Found %: C 26.65, 26.8; H 0.93, 0.94; Si 10.3, 10.13. $(Cl_4C_6HSiO_{1.5})_n$. Calculated %: C 26.98; H 0.37; Si 10.47.

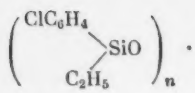
e) Hydrolysis of trichloro(2,3,4,5,6-pentachlorophenyl)silane. The hydrolysis was carried out similarly; 10 g (0.026 mole) of trichloro(2,3,4,5,6-pentachlorophenyl)silane was taken, and 5.4 g of polymer was obtained.

Found %: C 23.06, 22.6; H 0.66, 0.95; Si 8.85, 8.37; Cl 55.29, 55.16. $(Cl_5C_6SiO_{1.5})_n$. Calculated %: C 23.9; H—; Si 9.29; Cl 58.79.

II. Hydrolysis of Dichloro(chlorophenyl)ethylsilanes

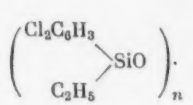
a) Hydrolysis of dichloro(4-chlorophenyl)silane. The hydrolysis was carried out as for the trichloro(chlorophenyl)silanes; 10 g (0.0417 mole) of dichloro(4-chlorophenyl)ethylsilane was taken and, after washing free from hydrochloric acid and distillation of solvent, we obtained 6.3 g of resinous polymer, soluble in organic solvents.

Found %: C 49.24, 49.90; H 3.29, 4.12; Si 14.47, 14.75; Cl 18.6, 18.8.
Calculated %: C 52.02; H 4.87; Si 15.18; Cl 19.2.



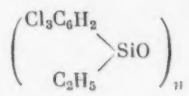
b) Hydrolysis of dichloro(2,4-dichlorophenyl)ethylsilane. The hydrolysis was carried out similarly; 10 g (0.036 mole) of dichloro(2,4-dichlorophenyl)ethylsilane was taken, and 7.1 g of resinous polymer was obtained.

Found %: C 41.24, 41.14; H 3.35, 3.27; Si 11.96, 12.36; Cl 32.3, 32.2.
Calculated %: C 43.85; H 3.65; Si 12.79; Cl 32.38.



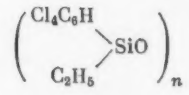
c) Hydrolysis of dichloroethyl(2,4,6-trichlorophenyl)silane. The hydrolysis was carried out similarly: 10 g (0.032 mole) of dichloroethyl(2,4,6-trichlorophenyl)silane was taken, and 6.4 g of polymer was obtained.

Found %: C 40.2, 40.4; H 2.61, 2.58; Si 12.65, 12.65; Cl 40.6, 40.3.
Calculated %: C 37.9; H 2.76; Si 11.03; Cl 41.97.



d) Hydrolysis of dichloroethyl(2,3,4,6-tetrachlorophenyl)silane. The hydrolysis was carried out similarly; 10 g (0.029 mole) of dichloroethyl(2,3,4,6-tetrachlorophenyl)silane was taken, and 4 g of polymer was obtained.

Found %: C 35.9, 35.5; H 1.90, 2.28; Si 10.23, 10.17.
Calculated %: C 33.35; H 2.08; Si 9.72.



III. Hydrolysis of Trichloro(chlorophenyl)silanes in an Alkaline Medium

a) Hydrolysis of trichloro(4-chlorophenyl)silane. A mixture of 30 g of water, 30 g of ether, and 5.14 g of chemically pure sodium hydroxide was prepared in the reaction flask. With vigorous stirring, 10 g (0.04 mole) of trichloro(4-chlorophenyl)silane in 20 ml of ether was added over a period of 3-5 minutes. When the addition was complete, stirring was continued for 30 minutes at 40°. The organic layer was separated from the aqeous layer, washed with water until neutral, and dried. The solution was filtered and ether was distilled off, first at atmospheric pressure, and then by exposure to a vacuum (15 mm) at 40°. The hydrolysis product (5 g) was a white brittle polymer, soluble in organic solvents.

Found %: C 41.02, 40.54; H 2.38, 2.66; Si 18.14, 17.89; Cl 20.7, 20.9. $(ClC_6H_4SiO_{1.5})_n$. Calculated %: C 44.05; H 2.44; Si 17.13; Cl 21.68.

b) Hydrolysis of trichloro(2,4-dichlorophenyl)silane. The hydrolysis was carried out similarly; 10 g (0.035 mole) of trichloro(2,4-dichlorophenyl)silane and 4.32 g of sodium hydroxide were taken, and 5 g of polymer was obtained.

Found %: C 36.9, 37.3; H 2.67, 2.49; Si 17.75, 17.79; Cl 28.8, 28.6. $(Cl_2C_6H_3SiO_{1.5})_n$. Calculated %: C 36.37; H 1.56; Si 14.15; Cl 35.85.

c) Hydrolysis of trichloro(2,4,6-trichlorophenyl)silane. The hydrolysis was carried out similarly; 10 g (0.031 mole) of trichloro(2,4,6-trichlorophenyl)silane and 3.84 g of sodium hydroxide were taken, and 5.4 g of brittle polymer was obtained.

Found %: C 27.47, 27.47; H 2.33, 2.20; Si 13.22, 13.64. $(Cl_3C_6H_2Si_{0.5})n$.* Calculated %: C 30.98; H 0.87; Si 12.05.

* As in original — Publisher's note.

d) Hydrolysis of trichloro(2,3,4,6-tetrachlorophenyl)silane. The hydrolysis was carried out similarly; 10 g (0.028 mole) of trichloro(2,3,4,6,-tetrachlorophenyl)silane and 3.55 g (0.088 mole) of sodium hydroxide were taken, and 5.9 g of polymer was obtained.

Found %: C 28.55, 28.27; H 1.01, 1.09; Si 12.78, 12.64. $(Cl_4C_6HSiO_{1.5})_n$. Calculated %: C 26.98; H 0.37; Si 10.47.

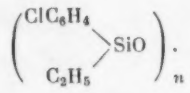
e) Hydrolysis of trichloro(2,3,4,5,6-pentachlorophenyl)silane. The hydrolysis was carried out similarly; 10 g (0.026 mole) of trichloro(2,3,4,5,6-pentachlorophenyl)silane and 3.24 g (0.081 mole) of chemically pure sodium hydroxide were taken, and 5.5 g of polymer was obtained.

Found %: C 23.19, 23.86; H 1.07, 1.04; Si 10.08, 10.25; Cl 55.6, 55.9. $(Cl_5C_6SiO_{1.5})_n$. Calculated %: C 23.9; H—; Si 9.29; Cl 58.79.

IV. Hydrolysis of Dichloro(chlorophenyl)ethylsilanes in an Alkaline Medium

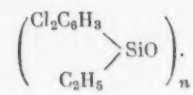
a) Hydrolysis of dichloro(4-chlorophenyl)ethylsilane. The hydrolysis was carried out as described for trichloro(4-chlorophenyl)silane. From 10 g (0.0417 mole) of dichloro(4-chlorophenyl)ethylsilane and 3.45 g (0.086 mole) of sodium hydroxide we obtained 6.8 g of a resinous polymer.

Found %: C 49.37, 49.46; H 4.61, 4.45; Si 16.03, 16.02; Cl 18.9, 18.3.
Calculated %: C 52.04; H 4.87; Si 15.18; Cl 19.2.



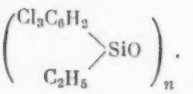
b) Hydrolysis of dichloro(2,4-dichlorophenyl)ethylsilane. The hydrolysis was carried out similarly; 10 g (0.036 mole) of dichloro(2,4-dichlorophenyl)ethylsilane and 3.0 g (0.075 mole) of sodium hydroxide were taken, and 7 g of polymer was obtained.

Found %: C 42.46, 42.32; H 3.13, 3.13; Si 13.19, 12.93; Cl 32.1, 32.2.
Calculated %: C 43.85; H 3.65; Si 12.79; Cl 32.32.



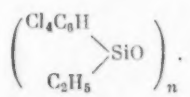
c) Hydrolysis of dichloroethyl(2,4,6-trichlorophenyl)silane. The hydrolysis was carried out similarly; 10 g (0.032 mole) of dichloroethyl(2,4,6-trichlorophenyl)silane and 2.68 g (0.067 mole) of sodium hydroxide were taken, and 6.4 g of polymer was obtained.

Found %: C 38.8, 38.7; H 1.99, 2.09; Si 11.71, 11.93; Cl 38.0, 38.5.
Calculated %: C 37.9; H 2.76; Si 11.04; Cl 41.97.



d) Hydrolysis of dichloroethyl(2,3,4,6-tetrachlorophenyl)silane. The hydrolysis was carried out similarly; 10 g (0.029 mole) of dichloroethyl(2,3,4,6-tetrachlorophenyl)silane and 2.44 g (0.061 mole) of sodium hydroxide were taken, and 6.1 g of resinous polymer was obtained.

Found %: C 36.5, 36.2; H 2.70, 2.48; Si 11.0, 11.09.
Calculated %: C 33.35; H 2.08; Si 9.72.



SUMMARY

1. The hydrolysis of trichloro(chlorophenyl)silanes in acid and alkaline media was investigated, and it was shown that no elimination of chloro-, dichloro-, trichloro-, tetrachloro-, or pentachloro-phenyl group occurs.

2. The hydrolysis of dichloro(chlorophenyl)ethylsilanes in acid and alkaline media was investigated, and it was shown that no elimination of the ethyl group or of the mono-, di-, tri-, or tetra-chlorophenyl group occurs.

LITERATURE CITED

[1] R. A. Benkeser, and H. R. Krysiak, J. Am. Chem. Soc. 75, 4528 (1953).

[2] I. C. Eaborn, J. Chem. Soc. Ost. 3148 (1953).

[3] B. H. Meen and H. Gilman, J. Org. Chem. 20, No. 1, 73 (1955).

[4] R. H. Krieble and I. R. Elliot, J. Am. Chem. Soc. 67, 1810 (1945).

[5] R. H. Krieble and I. R. Elliot, J. Am. Chem. Soc. 68, 2291 (1946).

[6] F. Whitmore and L. Sommer, J. Am. Chem. Soc. 68, 485 (1946).

[7] E. Larsson and L. Knopp, Acta. chem. scand. I, 268 (1947).

[8] H. Gilman, A. G. Brook and L. S. Miller, J. Am. Chem. Soc. 75, 4531 (1953).

[9] H. Gilman and L. S. Miller, J. Am. Chem. Soc. 73, 968 (1951).

[10] A. Ya. Yakubovich and G. V. Motsarev, J. Gen. Chem. 26, No. 2, 568 (1956).*

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ORGANOSILICON ESTERS OF ORGANOSILICON ACIDS

B. N. Dolgov, E. V. Kukharskaya, and D. N. Andreev

Only one organosilicon ester of an organosilicon acid has been described in the literature – triphenylsilyl triphenylsilanecarboxylate $(C_6H_5)_3SiCOOSi(C_6H_5)_3$, which was prepared recently by Brook [1] by reaction between triphenylsilanecarboxylic acid and chlorotriphenylsilane. As such organosilicon esters can be used as intermediaries in various preparative syntheses, we synthesized several esters of this type and studied their properties. For this purpose we made use of the transacylation of organosilicon esters investigated previously by Anderson and Stanislow [2] for the case of reaction of mono- and bis-acyloxysilanes with various organic acids, e.g., chloroacetic, 2-chloropropionic, 2-bromopropionic, and 3-iodopropionic acids.

The transacylation was carried out by heating organosilicon esters of propionic acid previously synthesized by us [3] with mono- and di-basic organosilicon acids, namely, (trimethylsilyl)propionic, (diethylmethylsilyl)-propionic, 3,3'-(tetramethyldisiloxanylene)dipropionic, and 3,3'-(tetraethyldisiloxanylene)dipropionic acids:

$$CH_3CH_2COOSi\cdot R_3 + R'_3SiCH_2CH_2COOH \rightarrow R'_3SiCH_2CH_2COOSiR_3 + CH_3CH_2COOH;$$
$$2CH_3CH_2COOSiR_3 + [HOOCCH_2CH_2SiR'_2]_2O \rightarrow [R_3SiOOCCH_2CH_2SiR'_2]_2O + CH_3CH_2COOH$$

The yields of organosilicon esters of organosilicon acids were 40.75%. The constants of the five esters synthesized are given in the table.

Compound No.	Formula of compound	B. p. in °C (p in mm)	d_4^{20}	n_D^{20}	*MR* found	*MR* calculated
I	$(CH_3)_3SiCH_2\cdot CH_2COOSi(C_2H_5)_3$	112—114 (6)	0.8812	1.4372	77.46	77.71
II	$[(CH_3)_3Si\cdot CH_2CH_2COO]_2Si(CH_3)_2$	151.5 (3)	0.9407	1.4368	97.04	97.36
III	$CH_3(C_2H_5)_2SiCH_2CH_2COOSi(C_2H_5)_3$	137.5 (2)	0.8905	1.4473	86.61	86.97
IV	$[(C_2H_5)_3SiOOC\cdot CH_2CH_2Si(CH_3)_2]_2O$	170—172 (6)	0.9213	1.4405	145.13	143.78
V	$[(C_2H_5)_3SiOOC\cdot CH_2\cdot CH_2Si(C_2H_5)_2]_2O$	178—181(1)	0.9251	1.4480	162.91	162.30

As intermediate compounds we prepared the previously undescribed (diethylmethylsilyl)propionic acid and diethyl [(diethylmethylsilyl)methyl]malonate, and also 3,3'-(tetraethyldisiloxanylene)dipropionic acid. This last compound was obtained by the action of concentrated sulfuric acid on (diethylmethylsilyl)propionic acid.

The ability of concentrated sulfuric acid to bring about the condensation of organosilicon compounds with elimination of a methyl group and formation of compounds containing a siloxane linkage was first observed by Sommer [4] for the case of the condensation of some organosilicon compounds containing a trimethylsilyl group:

$$(CH_3)_3SiCH_2CH_2COOH \xrightarrow[H_2O]{H_2SO_4} [HOOCCH_2CH_2Si(CH_3)_2]_2O + 2CH_4.$$

This reaction, which is new to organosilicon chemistry, makes it possible to convert organosilicon compounds containing functional groups in the side chain in good yield into new types of organosilicon compounds containing a siloxane linkage and double the number of functional groups in the side chains. However, to what extent this reaction, which is of such interest from the preparative point of view, can be applied remained obscure, because Sommer and co-workers applied it only to organosilicon compounds containing trimethylsilyl groups. In the present investigation we showed that this reaction can be extended also to compounds containing the $CH_3(C_2H_5)_2Si-$ grouping and that under the action of sulfuric acid only the methyl group is eliminated:

$$CH_3(C_2H_5)_2SiCH_2CH_2COOH \xrightarrow[H_2O]{H_2SO_4} [HOOCCH_2CH_2Si(C_2H_5)_2]_2O + 2CH_4.$$

The reaction proceeded at room temperature and the yield of dicarboxylic acid was 83.7%.

EXPERIMENTAL

I. Triethylsilyl (Trimethylsilyl)propionate $(CH_3)_3SiCH_2CH_2COOSi(C_2H_5)_3$

A mixture of 14.6 g (0.10 mole) of (trimethylsilyl)propionic acid prepared by Sommer's method [5] and 24.0 g (0.13 mole) of triethylsilyl propionate [3] was prepared in a Favorsky flask and heated in a metal bath for six hours at 190-200°. During the heating propionic acid was driven off. Fractionation of the reaction products gave 10.9 g (41.9%) of the substance (I). Found M 251; 244; ester value 217; 227; Si 21.53%; calculated for $C_{12}H_{28}O_2Si_2$ M 260; ester value 215; Si 21.54%.

II. Dimethylsilylene Bis [(trimethylsilyl)propionate] $[(CH_3)_3SiCH_2CH_2COO]_2Si(CH_3)_2$

A mixture of 20.4 g (0.10 mole) of dimethylsilylene dipropionate [3] and 36.5 g (0.25 mole) of (trimethylsilyl)propionic acid was heated for five hours at 190-200°. In the course of the reaction 13.6 g of propionic acid was distilled off. Fractionation gave 20.8 g (59.5%) of (II). Found M 357; 348; ester value 330; 328; Si 24.20%; calculated for $C_{14}H_{32}O_4Si_3$ M 348.6; ester value 321.9; Si 24.15%.

III. Triethylsilyl (diethylmethylsilyl)propionate $CH_3(C_2H_5)_2SiCH_2CH_2COOSi(C_2H_5)_3$

A mixture of 24.0 g (0.13 mole) of triethylsilyl propionate and 17.3 g (0.10 mole) of (diethylmethylsilyl)-propionic acid (VII) was heated for five hours at 190-200°; 7.2 g of propionic acid was distilled off. Fractionation gave 22.0 g (76.1%) of (III). Found M 280; 283; ester value 191; 189; Si 18.63%; calculated for $C_{14}H_{32}O_2Si_2$ M 288.5; ester value 194.4; Si 19.45%.

IV. Bistriethylsilyl 3,3'-(Tetramethyldisiloxanylene)dipropionate $[(C_2H_5)_3SiOOCCH_2CH_2Si(CH_3)_2]_2O$

A mixture of 8.4 g (0.03 mole) of 3,3'-(tetramethyldisiloxanylene)dipropionic acid (m.p. 54°, b.p. 127° (10 mm) prepared by Sommer's method [4] and 24.0 g (0.13 mole) of triethylsilyl propionate was heated for six hours at 200-210°; 4.3 g of propionic acid was distilled off. Fractionation gave 9.0 g (58.8%) of (IV). Found M 512; 520; ester value 227; 230; Si 21.70%; calculated for $C_{22}H_{50}O_5Si_4$ M 506.9; ester value 221; Si 22.14%.

V. Bistriethylsilyl 3,3'-(Tetraethyldisiloxanylene)dipropionate $[(C_2H_5)_3SiOOCCH_2CH_2Si(C_2H_5)_2]_2O$

A mixture of 18.8 g (0.10 mole) of triethylsilyl propionate and 12.7 g (0.038 mole) of (VIII) was heated for six hours at 190-200°; 5.8 g of propionic acid was distilled off. Fractionation gave 7.9 g (37.1%) of (V). Found M 547; 551; ester value 218; 207; Si 19.30%; calculated for $C_{26}H_{58}O_5Si_4$ M 563.0; ester value 199; Si 19.94%.

VI. Diethyl [(Diethylmethylsilyl)methyl]malonate $CH_3(C_2H_5)_2SiCH_2CH(COOC_2H_5)_2$

Sodiomalonic ester was prepared from 1000 ml of absolute ethanol, 320.2 g (2.0 moles) of malonic ester and 42.6 g (1.85 g-atoms) of sodium, and 280 g (1.85 moles) of (chloromethyl)diethylmethylsilane (b.p. 153°; n_D^{20} 1.4400; d_4^{20} 0.8988) was added. The reaction and the subsequent treatment were carried out as described in the literature [5]. Fractionation gave 321 g (63.2%) of (VI); b.p. 141° (4 mm); n_D^{20} 1.4408; d_4^{20} 0.9681; found MR 74.92; M 268; Si 9.87%; calculated for $C_{13}H_{26}O_4Si$; MR 75.49; M 274.4; Si 10.23%.

VII. (Diethylmethylsilyl)propionic Acid $CH_3(C_2H_5)_2SiCH_2CH_2COOH$

A solution of 255.4 g of potassium hydroxide in 255 ml of water was heated to 90° in a flask fitted with reflux condenser, and 314 g (1.14 moles) of (VI) was added dropwise. Reaction was completed by heating the mixture for 90 minutes. The reaction mixture was evaporated almost to dryness in a porcelain dish, the precipitated salt was dissolved in 400 ml of water, and 597 ml of concentrated hydrochloric acid was added to the resulting solution. The upper layer of organosilicon acid was separated, the aqueous layer was extracted with ether, and the ether extracts were combined with the layer of organosilicon acid. The mixture was washed with water and dried with anhydrous copper sulfate; ether was distilled off. Vacuum fractionation gave 148.8 g (75.3%) of (VII); b.p. 138.5° (6 mm); n_D^{20} 1.4455; d_4^{20} 0.9306; found MR 49.61; acid value 326; Si 16.23%; calculated for $C_8H_{18}O_2Si$ MR 49.37; acid value 323.7; Si 16.19%.

VIII. 3,3'-(Tetraethyldisiloxanylene)dipropionic Acid $[HOOCCH_2CH_2Si(C_2H_5)_2]_2O$

Concentrated sulfuric acid (98 ml) was introduced into a flask fitted with reflux condenser, mechanical stirrer, and dropping funnel, and 96.6 g of (VII) was added dropwise over a period of one hour. Reaction was accompanied by rise in temperature and evolution of gas. In order to complete reaction the mixture was stirred at room temperature until gas evolution ceased (1.5-2 hours). The reaction mixture was poured into a beaker containing ice, and crystals of (VIII) (which is liquid at room temperature) were precipitated. The dibasic acid was extracted with ether, and the extract was dried with calcium chloride. Ether was distilled off, and fractionation of the residue gave 70.0 g (83.7%) of (VIII), b.p. 154-155° (4 mm); n_D^{20} 1.4645; d_4^{20} 1.0356; found MR 89.21; acid value 334; 337; Si 17.05%; C 49.79%; H 8.98%; calculated for $C_{14}H_{30}O_5Si_2$ MR 89.06; acid value 335.4; Si 16.78%; C 50.27%; H 9.04%.

SUMMARY

1. Five new organosilicon esters of organosilicon acids were prepared by the transacylation of trialkylsilyl propionates with mono- and di-basic organosilicon acids.

2. For use as intermediaries we synthesized (diethylmethylsilyl)propionic acid, diethyl [(diethylmethylsilyl)methyl]malonate, and 3,3'-(tetraethyldisiloxanylene)dipropionic acid.

3. It was shown that treatment of (diethylmethylsilyl)propionic acid with concentrated sulfuric acid at room temperature results in rupture of the CH_3-Si bond and formation in good yield of 3,3'-(tetraethyldisiloxanylene)dipropionic acid.

LITERATURE CITED

[1] A. G. Brook, J. Am. Chem. Soc. 77, 4827 (1955).

[2] H. H. Anderson and G. M. Stanislow, J. Org. Chem. 18, 1716 (1953).

[3] D. N. Andreev, B. N. Dolgov and E. V. Kukharskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, No. 3, 528.

[4] L. H. Sommer, N. S. Marans, G. M. Goldberg, J. Rockett and R. P. Pioch, J. Am. Chem. Soc. 73, 882 (1951).

[5] L. H. Sommer, J. R. Gold, G. M. Goldberg and N. S. Marans, J. Am. Chem. Soc. 71, 1509 (1949).

Institute of Silicate Chemistry of
the Academy of Sciences of the USSR

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MECHANISM OF HALOMETHYLATION

I. N. Nazarov* and A. V. Semenovsky

The halomethylation reaction has been known for about sixty years [1], but even now the question of the mechanism of this process cannot be regarded as solved. For a long time it was considered that the agent in chloromethylation is bischloromethyl ether on the grounds that, on the one hand, it has been isolated in the reaction between paraformaldehyde and hydrogen chloride and, on the other hand, in presence of anhydrous zinc chloride bischloromethyl ether is able to give chloromethyl derivatives [2]. The possibility of carrying out chloromethylation with methylene chloride was examined, clearly because this might be supposed to be formed by the scission of bischloromethyl ether by hydrogen chloride. It was found, however, that methylene chloride is unable to give chloromethyl derivatives [3]. It was suggested also that chloromethylation proceeds by addition of the hypothetical chloromethyl alcohol at a double bond of the benzene ring with subsequent elimination of a molecule of water [4] – a very unlikely mechanism. On the basis of a comparison of reaction rates it was suggested [5] that chloromethylation is a reaction of the aromatic electrophilic-substitution type. The present authors showed recently [6] that the relative amounts of the isomers formed in chloromethylation are in accord with the laws that have been established for electrophilic substitutions (nitration, halogenation, etc.). This fact provides a sound basis for the assertion that chloromethylation is an electrophilic-substitution reaction.

Such a reaction mechanism implies the presence of a cation, reaction which with the aromatic nucleus results in replacement of hydrogen. A classical case of aromatic electrophilic substitution is that of nitration, in which the nitration agent is the nitronium cation $\overset{+}{N}O_2$. For chloromethylation it is possible to suggest two ionic mechanisms giving a chloromethyl derivative and requiring positive ions as agents. The first scheme [7] envisages the direct formation of the chloromethyl cation $\overset{+}{C}H_2Cl$ as chloromethylation agent:

$$H_2C=O + HCl \rightarrow OH-CH_2-Cl \rightleftarrows \overset{+}{C}H_2Cl + \overset{-}{O}H;$$

$$ArH + \overset{+}{C}H_2Cl \rightarrow ArCH_2Cl + H^+.$$

We do not regard this scheme as very probable, since it should lead to the formation of methylene chloride CH_2Cl_2, which, as we showed in special experiments, is not formed at all under chloromethylation conditions. The second ionic mechanism must therefore be regarded as the more probable; chloromethylation is then considered to occur with participation of the hydroxymethyl cation $\overset{+}{C}H_2OH$ [8], which first gives hydroxymethyl derivatives, which are then converted into chloromethyl derivatives under the chloromethylation conditions (action of hydrogen chloride):

$$H_2C=O + HCl \rightleftarrows \overset{+}{C}H_2OH + Cl^-.$$

$$ArH + \overset{+}{C}H_2OH \rightarrow ArCH_2OH + H^+.$$

$$ArCH_2OH + HCl \rightarrow ArCH_2Cl + H_2O.$$

Special experiments on the chloromethylation of benzyl alcohols showed that hydroxyl is completely replaced by chlorine under the conditions of this reaction. A powerful argument in favor of the hydroxymethyl-ion mechanism of halomethylation lies in the fact, which we established, that the bromo- and chloro-methylation

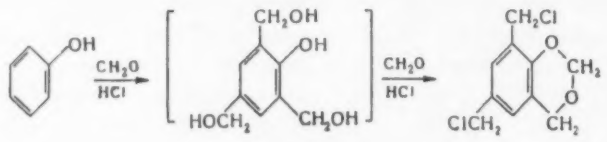
* Deceased.

of toluene, ethylbenzene, and cumene give absolutely identical relative amounts of o- and p-isomers [9]. These reactions, therefore, must have a common mechanism and initiating agent, and the latter must be the hydroxymethyl cation. If halomethylation proceeded with participation of halomethyl ions, then on steric grounds the bromomethylation of toluene, ethylbenzene, and cumene should result in the formation of more p-isomer than in the case of chloromethylation [10].

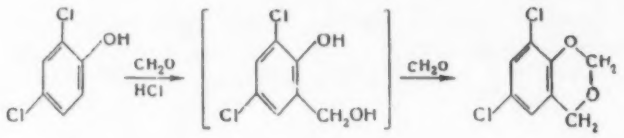
The hydroxymethyl-ion mechanism of halomethylation is confirmed also by the existence of the following equilibria in an acid medium, which indicate the presence of the hydroxymethyl cation [11]:

pH	Equilibrium
below 2.6	$H_2C(OH)_2 \rightleftarrows H_2\overset{+}{C}-OH + \overline{O}H$
2.6-4.5	$H_2C(OH)_2 \rightleftarrows H_2C\overset{+}{=}\overline{O} + \overline{O}H + H^+$
below 4.5	$H_2C(OH)_2 \rightleftarrows H_2C(OH)\overline{O} + H^+$

It is well known also that, by the action of formaldehyde on aromatic compounds in presence of acids, it is possible to effect the direct synthesis of aromatic hydroxymethyl derivatives, which, in presence of a second hydroxy group, often give the corresponding cyclic methylene ethers. For example, the chloromethylation of phenol [12] proceeds via the intermediate formation of the trishydroxymethyl derivative and gives a bicyclic methylene ether:



The chloromethylation of 2,4-dichlorophenol proceeds similarly [13] with intermediate formation of a hydroxymethyl derivative, which then gives a bicyclic methylene ether:



The question of the mechanism of halomethylation with the aid of halomethyl ethers in presence of anhydrous zinc chloride requires a special investigation. It is very probable that, under the reaction conditions, halomethyl ethers undergo scission or hydrolysis (which is facilitated by the presence of zinc chloride) with formation of the same reaction agents as in the case of direct halomethylation. In this connection it is interesting that chloromethyl methyl ether reacts with formation of chloromethyl derivatives appreciably more readily in presence of concentrated sulfuric acid, than in the presence of anhydrous zinc chloride [2].

EXPERIMENTAL

Reaction of paraform with hydrogen chloride, and the chloromethylation of toluene. Hydrogen chloride was passed for 14 hours into a vigorously stirred mixture of 30 g of paraform and 90 ml of concentrated hydrochloric acid at 55-56° in a three-necked flask fitted with stirrer and a trap for readily volatile substances (coil and receiver cooled to -18°). In the course of this time 3.7 g of bischloromethyl ether, b.p. 98-100°, condensed in the receiver; it gradually dissolved in water with formation of formaldehyde (hydrolysis). Absolutely no methylene chloride is formed in the reaction between paraform and hydrogen chloride.

After stirring of the reaction mixture had been continued for 14 hours, 69 g of toluene was added and stirring was continued further at 55-56° for 25 hours. The organic layer was then separated, washed with water,

with sodium bicarbonate solution, again with water, and dried over calcium chloride. Fractionation gave 1.8 g of head fraction and 77.6 g (73.7%) of a mixture of chloromethyl derivatives of toluene, b.p. 80-81° (12 mm). The residue from the distillation amounted to 4.4 g. This yield is the highest attainable in the chloromethylation of toluene under these conditions.

Chloromethylation of benzyl alcohol. Hydrogen chloride was passed for 40 minutes into a vigorously stirred mixture of 100 ml of carbon tetrachloride, 15 g of paraform, and 10 g of anhydrous zinc chloride. Addition was then made of 27 g of benzyl alcohol, and the mixture was stirred at 50° for 8.5 hours. In the middle of the experiment a further 10 g of zinc chloride was added. The product was washed – with water, with sodium bicarbonate solution, and again with water – and dried over potassium carbonate. Distillation gave 14.2 g of benzyl chloride, b.p. 79-81° (24 mm). From the partially solid residue we isolated 6.1 g of α,α'-dichloro-p-xylene, m.p. 97-99°, undepressed by admixture of a known sample. Distillation of the residual mother liquor gave 6 g of a liquid mixture of o-, m-, and p-isomers of α,α'-dichloroxylene, b.p. 100-115° (6 mm) and n_D^{18} 1.5660. The residue from the distillation amounted to 3.4 g.

Chloromethylation of benzyl acetate. Hydrogen chloride was passed for one hour into a vigorously stirred mixture of 200 ml of carbon tetrachloride, 20 g of paraform, and 20 g of anhydrous zinc chloride. Benzyl acetate (75 g) was then added, and stirring was continued at 50° for three hours, after which the reaction mixture was washed – with water, with sodium bicarbonate solution, and again with water – and dried over potassium carbonate. Fractionation gave 48 g (76%) of benzyl chloride, b.p. 50-60° (10 mm), and 1.63 g of crystalline α,α'-dichloro-p-xylene, m.p. 97-99°, was isolated from the residue. After separation of the crystals, the liquid residue (13.9 g) boiled over a wide range (120-210° at 10 mm) and appeared to be a complex mixture of various compounds, which were not investigated further.

Chloromethylation of ar-Methylbenzyl alcohols. Hydrogen chloride was passed for 24 hours into a vigorously stirred mixture of 20 g of paraform, 90 ml of concentrated hydrochloric acid, and 51.3 g of the mixture of ar-methylbenzyl alcohols obtained by hydrolysis of the chloromethylation product from toluene; the reaction temperature was about 55°. The organic layer was washed in the usual way, dried with magnesium sulfate, and vacuum-distilled. The product isolated, obtained in a yield of 50 g (85%), consisted of the original chloromethyl derivatives of toluene, b.p. 79-80° (12 mm) and $n_D^{17.5}$ 1.5600.

SUMMARY

The mechanism of the halomethylation of aromatic compounds is discussed, and arguments, based on experiment, are advanced in favor of a hydroxymethyl-ion mechanism for these reactions.

LITERATURE CITED

[1] G. Grassi, and C. Maselli, Gazz. 28, 11, 477 (1898).

[2] H. Stephen, W. F. Short, and G. Hadding, J. Chem. Soc. 117, 510 (1920).

[3] G. Lock, Ber. 74, 1568 (1941).

[4] J. F. Walker, Formaldehyde, N. Y., 1944, see p. 231.

[5] H. H. Izmant, and J. Dudek, J. Am. Chem. Soc. 71, 3763 (1949).

[6] I. N. Nazarov and A. V. Semenovsky, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1957,* 100.

[7] O. Wichterle, and J. Cerny, Chem. Listy 49, 1038 (1955).

[8] Sukh Dev, J. Ind. Chem. Soc. 32, 403 (1955).

[9] I. N. Nazarov and A. V. Semenovsky, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1957,* 212.

[10] I. N. Nazarov and A. V. Semenovsky, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1957,* 840.

[11] M. Wadano, C. Trogus, and K. Hess, Ber. 67, 174 (1934).

[12] British Patent 347887 (1931); French Patent 695602 (1930); C. 1932, I, 103, 2997.

[13] E. Ziegler, et al., Ber. 74, 1871 (1941).

N. D. Zelinsky Institute of Organic Chemistry
of the Academy of Sciences of the USSR

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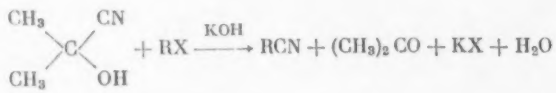
PREPARATIVE METHOD FOR THE SYNTHESIS OF NITRILES FROM 2-METHYLLACTONITRILE

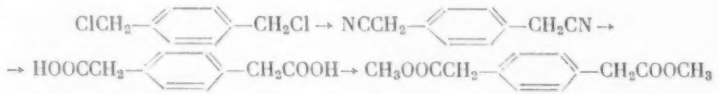
I. N. Nazarov*, A. V. Semenovsky, and A. V. Kamernitsky

We have previously reported [1, 2] the development of preparative syntheses for various nitriles with the aid of 2-methyllactonitrile (acetone cyanohydrin) as a source of hydrogen cyanide. In this way we succeeded in preparing, in good yields, addition products of hydrogen cyanide at an activated double bond [1] and also cyanohydrins of aldehydes and ketones [2]. It was considered desirable to also investigate the possibility of using 2-methyllactonitrile in the replacement of halogens by the cyano group:



(X = Cl or Br). As is well known, the usual methods of obtaining nitriles from halogen compounds are associated with the use of anhydrous hydrogen cyanide or of alkali-metal cyanides.

It was found that the success with which reaction can be effected between halogen compounds and 2-methyllactonitrile in an alkaline medium depends greatly on the character of the halogen compound used and the mobility of the halogen (see table). Thus, whereas ethyl and allyl bromides give low yields of nitriles, compounds of the benzyl chloride type give the corresponding nitriles in 70-80% yield and analogous compounds of the benzyl bromide type give the same nitriles in 80-85% yield in two hours at room temperature. The difference in the readiness with which chloromethyl and bromomethyl derivatives of aromatic compounds react is considerable. Special experiments on the reaction of mixtures of such compounds with 2-methyllactonitrile showed that, when the content of chloro compound is 50% and less, reaction is mainly with the bromo compound during the first two hours at room temperature and the residual chloro compound reacts only during subquent heating of the mixture. This fact makes it possible to estimate the composition of mixtures containing not more than 50% of chloro compound from the amount of potassium bromide formed at first and the amount of potassium chloride formed later. When the content of chloro compound is high, the selectivity of the reaction is no longer maintained, i.e., potassium chloride begins to separate along with potassium bromide. An attempt at the selective replacement of only one of two equivalent halogens was not successful. Thus, reaction between α,α'-dichloro-p-xylene and one half of the theoretical amount of 2-methyllactonitrile gave a mixture, which evidently consisted of the original dichloro compound, the chloro nitrile, and the dinitrile. In most cases reaction with 2-methyllactonitrile was carried out with the mixture of o- and p-isomers obtained in the halomethylation of a benzene derivative. The products were mixtures of the corresponding nitriles, which generally had wide ranges of boiling point. However, when pure p-halomethyl derivatives were used, pure p-substituted phenylacetonitriles were obtained and had the constants reported in the literature. In the case of α,α'-dichloro-p-xylene, the corresponding dinitrile was converted into the acid, which was itself converted into its dimethyl ester:



* Deceased.

The results of the investigation are presented in the following table.

No.	Original halogen compound	Nitrile obtained	Yield %
1	C_2H_5Br	C_2H_5CN	11
2	$CH_2=CH-CH_2Br$	$CH_2=CH-CH_2CN$	30
3	$C_6H_5CH_2Cl$	$C_6H_5CH_2CN$	65
4	$CH_3C_6H_4CH_2Cl$	$CH_3C_6H_4CH_2CN$	69
5	$C_2H_5C_6H_4CH_2Cl$	$C_2H_5C_6H_4CH_2CN$	80
6	$(CH_3)_2CHC_6H_4CH_2Cl$	$(CH_3)_2CHC_6H_4CH_2CN$	90
7	p-$ClCH_2C_6H_4CH_2Cl$	p-$NCCH_2C_6H_4CH_2CN$	76
8	$C_2H_5OOCCH_2C_6H_4CH_2Cl$	$C_2H_5OOCCH_2C_6H_4CH_2CN$	57
9	$FC_6H_4CH_2Cl$	$FC_6H_4CH_2CN$	73
10	p-$ClC_6H_4CH_2Cl$	p-$ClC_6H_4CH_2CN$	77
11	$BrC_6H_4CH_2Cl$	$BrC_6H_4CH_2CN$	73
12	p-$JC_6H_4CH_2Cl$	p-$JC_6H_4CH_2CN$	70
13	$CH_3C_6H_4CH_2Br$	$CH_3C_6H_4CH_2CN$	84
14	$C_2H_5C_6H_4CH_2Br$	$C_2H_5C_6H_4CH_2CN$	86
15	$(CH_3)_2CHC_6H_4CH_2Br$	$(CH_3)_2CHC_6H_4CH_2CN$	84

The high yields obtained in the reaction of 2-methyllactonitrile with halomethyl derivatives of aromatic compounds make it possible to recommend the reaction as a preparative method in which the use of highly toxic hydrocyanic acid or alkali-metal cyanides is avoided. It is possible that under more severe conditions this reaction may be carried out satisfactorily also with aliphatic halogen derivatives. It is known, for example, that in the usual preparation of 3-butenenitrile it is recommended that allyl halide should be heated with potassium cyanide in a sealed tube [3]. For reaction under milder conditions, however, copper cyanide may be used [4].

EXPERIMENTAL

Propionitrile. A mixture of 54.5 g of ethyl bromide, 42.5 g of 2-methyllactonitrile, 28 g of potassium hydroxide, and 10 ml of methanol was heated in a 250 ml rotating autoclave for one hour at 95-100°. The precipitate formed was filtered off, solvent was distilled off, the residue was extracted with ether, and the ether extract was dried with calcium chloride. Ether was distilled off, and distillation of the residue gave 3 g (11%) of propionitrile, b.p. 96-99° and n_D^{20} 1.3695.

3-Butenenitrile. A mixture of 36 g of allyl bromide, 25.5 g of 2-methyllactonitrile, and 170 ml of a 10% solution of potassium hydroxide in methanol was refluxed for three hours and then set aside overnight. On the next day the methanol was distilled off and the residue was diluted with water. The mixture was carefully extracted with ether, and the extract was dried with sodium sulfate and fractionated. The product, amounting to 6.7 g (30%), was 3-butenenitrile, b.p. 117-120°. The reaction product appeared to contain some crotononitrile, which was not isolated.

Phenylacetonitrile. A mixture of 12.6 g of benzyl chloride, 9 g of 2-methyllactonitrile, and 40 ml of 10% ethanolic sodium hydroxide was left overnight and then boiled for 30 minutes. Precipitated sodium chloride was filtered off, alcohol was distilled off, and the product was extracted with ether and vacuum-fractionated. Phenylacetonitrile, b.p. 99-100° (9 mm) was obtained in a yield of 7.6 g (65%). The following nitriles were prepared similarly.

Mixture of o- and p-tolylacetonitriles. A mixture of 14.0 g of the mixture of α,α'-dichloro-o- and p-xylenes obtained in the chloromethylation of toluene [5], 9 g of 2-methyllactonitrile, and 40 ml of 10% ethanolic sodium hydroxide gave 9.04 g (69%) of a mixture of nitriles of b.p. 111-114° (10 mm). The head fraction amounted to 5 g, and the residue to 0.5 g.

Mixture of o- and p-ethylphenylacetonitriles. A mixture of 15.5 g of the mixture of chloromethyl derivatives of ethylbenzene [6], 10.2 g of 2-methyllactonitrile, and 12 ml of 10 M KOH (aqueous) diluted with 70 ml of alcohol gave 11.6 g (80%) of a mixture of nitriles of b.p. 106-119° (8 mm). The head fraction amounted to 2.4 g and the residue to 0.5 g.

Mixture of o- and p-isopropylphenylacetonitriles. A mixture of 16.9 g of the mixture of chloromethyl derivatives of cumene [6], 10.2 g of 2-methyllactonitrile, 12 ml of aqueous 10 m KOH, and 90 ml of alcohol gave 12.8 g (80%) of a mixture of nitriles of b.p. 125-140° (15 mm). The head fraction amounted to 4.0 g, and the residue to 0.5 g.

p-Benzenediacetonitrile. A mixture of 5.2 g of α,α'-dichloro-p-xylene (m.p. 99-100.5°), 5.5 g of 2-methyllactonitrile, 6 g of 40% aqueous sodium hydroxide, 50 ml of alcohol, and 30 ml of dioxan gave 3.6 g (76%) of crystalline dinitrile, m.p. 95.5-97° (from alcohol), undepressed by admixture of a known sample. A mixture of 3.0 g of this dinitrile and 100 ml of concentrated hydrochloric acid was boiled for five hours and gave 3.52 g (94.3%) of the corresponding diacid, from which the dimethyl ester m.p. 55-56°, was prepared by the action of ethereal diazomethane. The literature gives 56° for the melting point of dimethyl p-benzenediacetate.

Mixture of o-, m-, and p-isomers of ethyl (α-cyanotolyl)acetate. A mixture of 4.24 g of the mixture of chloromethyl derivatives of ethyl phenylacetate [6], 2.0 g of 2-methyllactonitrile, 2 g of 40% aqueous sodium hydroxide, and 20 ml of alcohol gave 2.3 g (57%) of a mixture of nitriles, b.p. 98-100° (10 mm) and n_D^{20} 1.4975.

Mixture of o- and p-fluorophenylacetonitriles. A mixture of 14.5 g of the mixture of chloromethyl derivatives of fluorobenzene [6], 10.2 g of 2-methyllactonitrile, 12 ml of 10 M KOH, and 70 ml of alcohol gave 9.8 g (73%) of a mixture of nitriles, b.p. 102-108° (11 mm). The head fraction amounted to 1.5 g, and the residue to 0.8 g.

(p-Chlorophenyl)acetonitrile. A mixture of 16.1 g of p-chlorobenzyl chloride, m.p. 27-28° [6], 10.2 g of 2-methyllactonitrile, 12 ml of 10 M KOH, and 70 ml of alcohol gave 11.7 g (77%) of (p-chlorophenyl)acetonitrile, b.p. 130-134° (11 mm) and m.p. 28.0-29.5°. The head fraction amounted to 2.3 g, and the residue to 0.9 g.

Mixture of o- and p-bromophenylacetonitriles. A mixture of 20.5 g of the mixture of chloromethyl derivatives of bromobenzene [6], 10.2 g of 2-methyllactonitrile, 12 ml of 10 M KOH, and 70 ml of alcohol gave 14.4 g (73%) of a mixture of nitriles of b.p. 127-144° (10 mm). When this was cooled, crystals of m.p. 46-47° separated out; the melting point of (p-bromophenyl)acetonitrile is 46-47°. The head fraction amounted to 1.9 g, and the residue to 1.9 g.

(p-iodophenyl)acetonitrile. A mixture of 5.2 g of p-iodobenzyl chloride of m.p. 51.5-53.5° [6], 2.1 g of 2-methyllactonitrile, 2.5 ml of 10 M KOH, and 40 ml of alcohol gave 3.5 g (70%) of (p-iodophenyl)acetonitrile, b.p. 143-148° (6 mm) and m.p. 47.0-48.5°. The head fraction amounted to 0.5 g, and the residue to 0.6 g.

Mixture of o- and p-tolylacetonitriles from bromomethyl derivatives. The mixture of the bomomethyl derivatives of toluene [7] (18.5 g), 2-methyllactonitrile (10.2 g), and 10 M KOH (12 ml) were dissolved in 70 ml of alcohol. The mixture was set aside overnight, precipitated potassium bromide was filtered off, the alcoholic solution was dried with anhydrous magnesium sulfate, alcohol was distilled off, and the residue, in admixture with a little ether, was again dried with magnesium sulfate. Ether and a head fraction (2.2 g) were distilled off. Vacuum distillation gave 11.0 g (84%) of a mixture of nitriles b.p. 105-113° (8 mm); residue 0.6 g. The following nitriles were prepared similarly from bromomethyl derivatives.

Mixture of o- and p-ethylphenylacetonitriles. A mixture of 19.9 g of the mixture of bromomethyl derivatives of ethylbenzene [7], 10.2 g of 2-methyllactonitrile, 12 ml of 10 M KOH, and 80 ml of alcohol gave 12.5 g (86%) of a mixture of nitriles of b.p. 120-128° (11 mm). The head fraction amounted to 3.2 g, and the residue to 0.4 g.

Mixture of o- and p-isopropylphenylacetonitriles. A mixture of 11.5 g of the mixture of bromomethyl derivatives of cumene [7], 6 g of 2-methyllactonitrile, 7 ml of 10 M KOH, and 60 ml of alcohol gave 7.2 g (84%) of a mixture of nitriles of b.p. 126-133° (11 mm). The head fraction amounted to 1.0 g, and the residue to 0.5 g.

SUMMARY

In the reaction of 2-methyllactonitrile (acetone cyanohydrin) with halogen compounds of the benzyl

chloride and bromide types in presence of alkali, the corresponding phenylacetonitriles are formed in high yield (65-85%).

LITERATURE CITED

[1] I. N. Nazarov and S. I. Zavyalov, J. Gen. Chem. 24, 466 (1954).*

[2] I. N. Nazarov, A. A. Akhrem, and A. V. Kamernitsky, J. Gen. Chem. 25, 1345 (1955).*

[3] C. Pomeranz, Ann. 351, 357 (1907); A. Rinne, B. Tollens, Ann. 159, 106 (1871).

[4] Organic Syntheses, Collection 1 (Trans. from English), 1949, p. 500.

[5] I. N. Nazarov and A. V. Semenovsky, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1956,* 1487.

[6] I. N. Nazarov and A. V. Semenovsky, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1957,* 100.

[7] I. N. Nazarov and A. V. Semenovsky, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1957,* 212.

N. D. Zelinsky Institute of Organic Chemistry
of the Academy of Sciences of the USSR

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COPOLYMERIZATION OF CHLOROPRENE WITH VINYL ESTERS

COMMUNICATION 1

S. N. Ushakov and L. B. Trukhmanova

A fairly thorough study has been made of the copolymerization of chloroprene with many other unsaturated monomers, and in all the systems studied chloroprene was found to be considerably more active in free-radical copolymerization than the second monomer [1, 2].

In our investigation we studied the copolymerization of chloroprene with various vinyl esters (formate, acetate, propionate, and butyrate). There are no data in the literature on the possibility of forming copolymers between chloroprene and these monomers. The investigation had the object of developing a method of copolymerization, determining relative activities in the copolymerization of vinyl esters with chloroprene, and observing the character of the changes shown in a homologous series.

EXPERIMENTAL

1. Starting materials and copolymerization procedure. Well-purified freshly distilled monomers were used for the copolymerization. The chloroprene used had the following properties:

		Data in literature [3]	Found
B. p. (°C)	°C	59.4	59.4
Sp. gr (d_{20}^{20})	d_{20}^{20}	0.9583	0.9570—0.9583
Refractive index (n_D^{20})	n_D^{20}	1.4583	1.4580

The esters used for copolymerization had the following properties (Table 1).

TABLE 1

No.	Vinyl ester	B. p. (°C)		Sp. gr. (d_{20}^{20})		Refractive index (n_D^{20})	
		data in literature	found	data in literature	found	data in literature	found
1	Vinly formate [4]	46—46.5	45.9—46.1	0.9592	0.9600 0.9593	— 1.3956	1.3845
2	Vinly acetate [5]	72.5	72.4—72.7	0.9342			1.3959
3	Vinyl propionate [5]	95	93.7—94.2	—	0.9172	1.4120	1.4028
4	Vinyl butyrate [6] [5]	115 116.5	115	0.9315 0.8994	0.9315	1.411	1.4120

The copolymerization of chloroprene with vinyl formate, vinyl acetate, vinyl propionate, and vinyl butyrate was carried out in the mass at 65°. Benzoyl peroxide (0.2% on the total weight of monomers) was

used as initiator. The reactions were carried out in sealed tubes in a water or air thermostat. Polymerization was continued for 7-30 hours, until a viscous liquid or highly tenacious mass – depending on the degree of conversion – was obtained.

In the copolymerization of chloroprene with vinyl formate at high initial ester : chloroprene ratios (2:1 and greater), and also in certain cases of copolymerization of chloroprene with vinyl acetate (great excess of the ester and high conversion), copolymers were obtained which were insoluble in the monomer mixture and separation into layers occurred in the tubes with precipitation of insoluble copolymer. When the tubes were opened, the copolymers were reprecipitated two or three times to remove unchanged monomers and obtain the copolymers in a pure state. To prevent cross-linking of the copolymers, the antioxidant Neozone D was added to the copolymer solution. Benzene was generally used as solvent for copolymers of chloroprene and vinyl formate, but chloroform or acetone was used for copolymers containing a large amount of vinyl formate. Methanol was used as precipitant for all vinyl formate copolymers.

Copolymers of chloroprene with vinyl acetate were generally precipitated by addition of the benzene solution to methanol. Copolymers containing a large amount of vinyl acetate were precipitated from benzene solution by a large excess of diethyl ether or from methanol or acetone solutions by a large excess of water. Copolymers of chloroprene with vinyl propionate and vinyl butyrate were precipitated from benzene solution by methanol, except in the case of one copolymer of chloroprene with vinyl butyrate, which was precipitated from benzene solution by a mixture of methanol and water (2:3). The copolymer solutions for precipitation had concentrations of about 5%. The precipitant was taken in 6-8 fold excess over the volume of solution.

In each case, after separation of the copolymer precipitate the filtrate was checked for completeness of precipitation by evaporation. Checking for completeness of precipitation is particularly important for copolymers of chloroprene with vinyl acetate, vinyl propionate, and vinyl butyrate, because these copolymers gradually acquire solubility in methanol as their ester contents increase. The precipitated copolymers were dried to constant weight in a vacuum drier at a residual pressure of 2-10 mm, first at room temperature and then at 30-40°. The copolymers dried out extremely slowly and sometimes required 1-2 months.

In the copolymerization the conversion was determined gravimetrically from the yield of purified copolymers, dried to constant weight. The composition of these purified copolymers was determined from the chlorine content. Chlorine contents were determined by the Carius method or by a micromethod based on heating the substance with lime and potassium [7].

2. Determination of Copolymerization Constants. For the calculation of copolymerization constants for all the systems investigated it is essential to select a general method giving the most accurate values. Copolymerization constants were determined by us by various methods, including a) a method based on the graphical solution of the integral equation for the composition of the copolymer [8]; b) a method based on a simplified differential equation for the composition with one unknown, it being assumed that the rate of addition of vinyl formate monomer to its radical is so low in comparison with the rate of addition of chloroprene monomer to this radical that $r_1 \approx 0$; and c) a method based on paired solutions of the differential equation for composition for several pairs of original ratios.

The results of the calculations of constants by these methods were not satisfactory, and we therefore tried to determine copolymerization constants for the systems studied by the method of the selected curve [9]. The experimental copolymerization curve for various original compositions was constructed in the coordinates of copolymer composition and original mixture composition, and curves calculated from the differential equation for composition were plotted on the same graph for different values of r_1 and r_2. For the copolymerization constants of the system, those values of r_1 and r_2 were selected that gave a calculated copolymerization curve that fitted best to the experimental points. The result of the selection of calculated curves for the systems formed by chloroprene with vinyl formate, vinyl acetate, vinyl propionate, and vinyl butyrate is shown in Tables 2-5 and Figures 1-4.

The copolymerization constants found for all four systems by the method of the selected curve are given in Table 6.

It will be seen from Tables 2-6 that in all the systems investigated the copolymerization constant of the ester is determined to a very low degree of accuracy, which is however permissible for copolymerization constants having such a low absolute value. Dozens of systems are described in the literature in which one of the

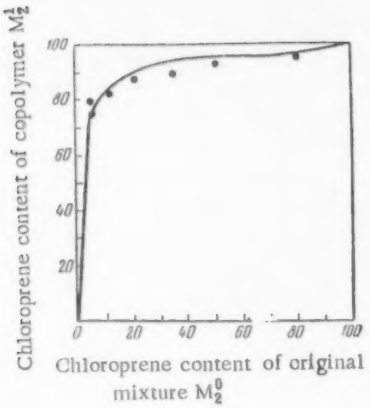

Fig. 1. Curve for the copolymerization of chloroprene with vinyl formate: ● – experimental points; ——— — curve calculated for $r_1 = 0.01$, $r_2 = 30$.

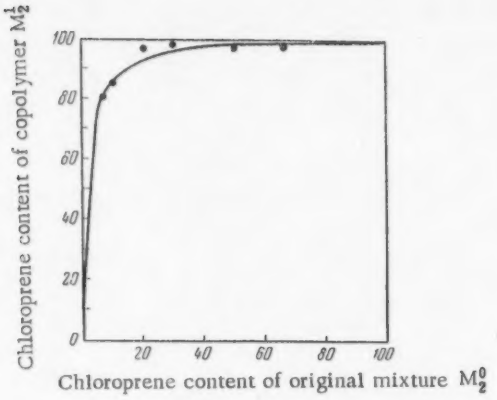

Fig. 2. Curve for the copolymerization of chloroprene with vinyl acetate: ● – experimental points. ——— – curve calculated for $r_1 = 0.01$, $r_2 = 50$.

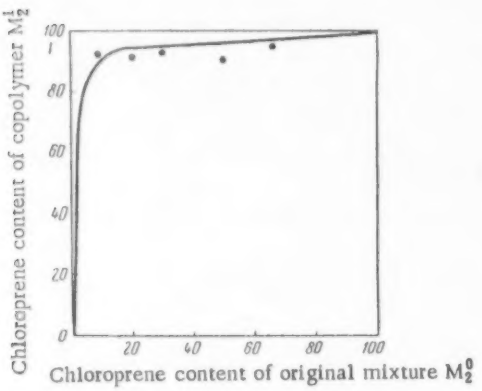

Fig. 3. Curve for the copolymerization of chloroprene with vinyl propionate: ●– experimental points: ——— — curve calculated for $r_1 = 0.05$, $r_2 = 70$.

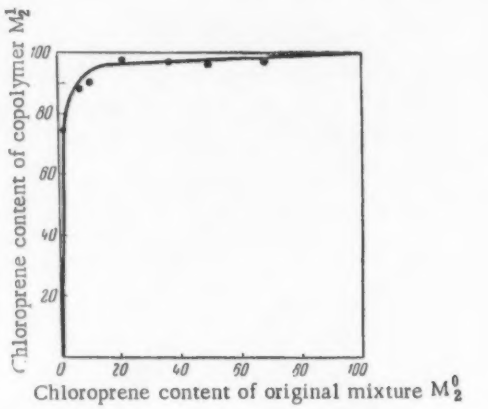

Fig. 4. Curve for copolymerization of chloroprene with vinyl butyrate: ● – experimental points; ——— — curve calculated for $r_1 = 0.02$, $r_2 = 90$.

constants, which is very small in absolute value, is determined with a possible error of about 100%. It is therefore more correct to consider that the true values of the copolymerization constants lie within the limits indicated.

The values found for the copolymerization constants of all these systems indicate that a polymeric radical terminating with an ester unit reacts much more rapidly with chloroprene monomer than with ester monomer, whereas a polymeric radical terminating with a chloroprene unit also reacts more readily with chloroprene monomer than with ester monomer. Hence the tendency to produce alternation of units is manifested only be one of the components – the ester; the copolymer always contains more chloroprene than the original mixture.

When copolymerization constants are compared for the homologous series of vinyl esters, it is seen that, with increase in the molecular weight of the acid residue of the ester, r_2 increases (the change in r_1 is obscured

by the low accuracy in the determination of r_1). This picture is in conflict with some of the results reported in the literature.

Argon and Alfrey [10], in a study of the copolymerization of methyl methacrylate, ethyl methacrylate, and butyl methacrylate with vinyldene chloride found that the length of the ester grouping has only a slight effect on the polymerization constants. Other investigations, however, indicate the opposite. Thus, Chapin, Ham, and Mills [11], in a comparison of the copolymerization of vinyl formate, vinyl acetate, vinyl benzoate, and vinly 2-ethylhexanoate with acrylonitrile, found that the copolymerization constants of vinyl esters with respect to the acrylonitrile radical diminish as the chain of the ester is lengthened, but the copolymerization constant of acrylonitrile increases under these circumstances. Ushakov and Nikolaev [12], in a study of the copolymerization of vinylcarbazole with the vinyl esters that we have used in this work, found that, as the chain of the ester becomes more complex, r_1 and r_2 diminish.

TABLE 2

Determination of Polymerization Constants for the System Chloroprene (M_2) and Vinyl Formate (M_1) by the Method of the Selected Curve

r_1	r_2	Chloroprene content of the copolymer (M_2^1) for a chloroprene content of the original mixture M_2^0 (moles %) of					
		80	50	30	20	10	5
0	20	98.78	95.45	90.54	85.71	77.55	67.24
0.005	25	99.0	96.28	92.06	87.75	78.33	
0.005	30	99.17	96.87	93.15	89.28	80.57	70.02
0.01	30	99.17	96.84	92.91	89.04	79.9	68.6
Experimental data		95.55	92.68	89.5 for $M_0 = 35$	89.0	83 87 80	80.5

TABLE 3

Determination of Polymerization Constants for the System Chloroprene (M_2) and Vinyl Acetate (M_1) by the Method of the Slected Curve

r_1	r_2	Chloroprene content of the copolymer (M_2^1) for a chloroprene content of the original mixture M_2^0 (moles %) of					
		80	50	30	20	10	5
0	40	99.38	97.62	94.78	91.67	85.40	
0.01	60	99.58	98.37	96.31	93.9	87.55	
0.01	50	99.46	98.02	95.63	92.84	85.73	75.32
Experimental data		$M_2^0 = 66$ $M_2^1 = 98.5$	97.3	98.1	96.3	85.0	

The differences indicated in the behavior of the systems mentioned are probably to be explained by the difference in the nature of the components – vinylcarbazole being an ethylenic compound, whereas chloroprene has a conjugated system of double bonds. The difference in behavior of free radicals having one and two double

TABLE 4

Determination of Polymerization Constants for the System Chloroprene (M_2) and Vinyl Propionate (M_1) by the Method of the Selected Curve

r_1	r_2	Chloroprene content of the copolymer (M_2^1) for a chloroprene content of the original mixture M_2^0 (moles %) of				
		80	50	30	20	10
0.05	60	99.58	98.3	95.99	93.02	84.1
0.03	70	92.64	98.56	96.66	94.29	87.36
0.05	70	99.64	98.51	96.52	94.00	85.82
Experimental data		$M_2^0 = 67$ $M_2^1 = 96.72$	90.39	93.58	91.34	91.89

TABLE 5

Determination of Polymerization Constants for the System Chloroprene (M_2) and Vinyl Butyrate (M_1) by the Method of the Selected Curve

r_1	r_2	Chloroprene content of the copolymer (M_2^1) for a chloroprene content of the original mixture M_2^0 (moles %) of				
		80	50	30	20	10
0.05	90	99.72	98.86	97.26	94.14	88.35
0.01	90	99.72	98.87	97.47	95.78	90.96
0.005	80	99.69	98.77	97.22	95.37	91.32
0.02	90	99.72	98.89	97.34	95.62	90.30
Experimental data		$M_2^0 = 70$ $M_2^1 = 98.5$	98.36	97.93	96.65	$M_2^0 = 6.9$ 90.41 $M_2^1 = 88.96$

bonds has received very little study. It has therefore not been found possible to explain the difference in the behavior of these substances in copolymerization with a series of vinyl esters by difference in the distribution of electron density in the radicals and molecule, although it is probable that this is where the explanation is to be sought.

On the basis of the copolymerization constants determined by the method of the selected curve we calculated the activities of the vinyl esters investigated with respect to the chloroprene radical.

It will be seen from Fig. 7 that the relative activities of vinyl esters toward the chloroprene radical diminish along the homologous series with increase in the molecular weight of the acid residue of the ester.

3. Calculation of integral and differential compositions of copolymers of chloroprene with vinyl formate. For calculation of the composition of the copolymer obtained at a given conversion we used the approximate integral equation for composition (1) of Medvedev and Abkin [13]:

$$\frac{M_1}{M_1^0} = \left[\frac{M_2}{M_2^0}\right]^K, \qquad (1)$$

$$K = \frac{r_1 \cdot \frac{M_1^0}{M_2^0} + 1}{r_2 + \frac{M_1^0}{M_2^0}}; \qquad (2)$$

in which

in the corrected form [14], in which

$$K_{int} = \frac{K_0 + K_\alpha}{2}. \qquad (3)$$

On the basis of the calculated values of differential and integral compositions of the copolymer we constructed diagrams for the state of the system containing curves of integral and differential composition for three compositions of the original mixture (Figs. 5 and 6). Such diagrams make it possible to characterize all possible cases of the behavior of the components of the given pair for any possible relative amounts in the reaction mixture.

TABLE 6

Copolymerization Constants for the Systems Chloroprene (M_2) and Vinyl Formate (M_1), Chloroprene (M_2) and Vinyl Acetate (M_1), Chloroprene (M_2) and Vinyl Propionate (M_1), and Chloroprene (M_2) and Vinyl Butyrate (M_1).

System M_1 — M_2	r_1	r_2
Vinyl formate — chloroprene	0.01±0.01	30±5
Vinyl acetate — chloroprene	0.01±0.01	50±10
Vinyl propionate — chloroprene	0.05±0.05	70±10
Vinyl butyrate — chloroprene	0.02±0.02	90±2

4. Some Properties of the Copolymers. a) Solubility of copolymers of chloroprene with vinyl formate. The solubilities of these copolymers vary greatly with composition. They are all soluble in chloroform. Like pure polychloroprene, copolymers containing 80-96% moles % of chloroprene are soluble in benzene, dichloroethane, carbon tetrachloride dioxan , and pyridine, but are insoluble in ethanol and methanol. Unlike polychloroprene, they have partial solubility in acetone. Copolymers containing 5-10 moles % of chloroprene are soluble in hot acetone, in dioxan , and in chloroform, but are insoluble in benzene, dichloroethane, methanol, and ethanol. When they are kept, even with addition of antioxidant, the copolymers become less soluble as a result of aging. Introduction of ester units into the chain of polychloroprene somewhat improves its solubility.

In the copolymerization of chloroprene with vinyl formate a higher conversion can be attained with preservation of the solubility of the product than in the polymerization of pure chloroprene. Thus, in the polymerization of chloroprene an insoluble polychloroprene (the μ-form) is formed already at 25-30% conversion, but in copolymerization with vinyl formate a conversion of about 40% can be attained with formation of a soluble product containing 8-9% of vinyl formate.

TABLE 7

Relative Activities of Monomer ($\frac{1}{r}$) Toward Various Radicals

Monomer	Radical				
	chloroprene	vinyl formate	vinyl acetate	vinyl propionate	vinyl butyrate
Chloroprene	1.0	100	100	20	50
Vinyl formate	0.0333	1.0			
Vinyl acetate	0.02		1.0		
Vinyl propionate	0.0142			1.0	
Vinyl butyrate	0.0111				1.0

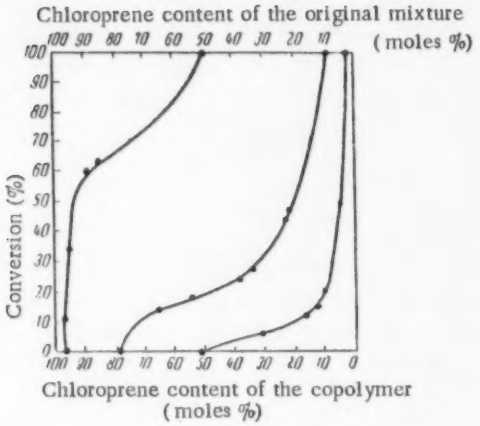

Fig. 5. Diagram of integral composition of copolymers calculated for various compositions of the original mixture and various conversions.

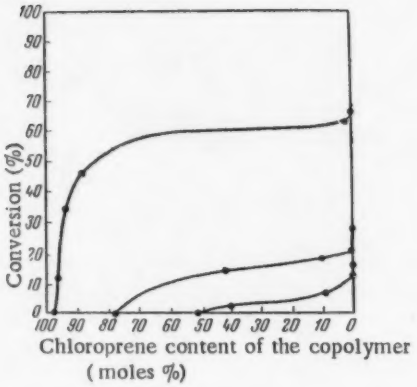

Fig. 6. Diagram of differential composition of copolymers calculated for various compositions of the original mixture and various conversions.

TABLE 8

Glass Points of Copolymers

Composition of copolymer	Chloroprene content of copolymer (moles %)	Glass point T_G (°C)
Polychloroprene	100	—43.5
Copolymer of chloroprene with vinyl formate	96	—45.2
Ditto	86	—40.7
"	70	—40.2
Copolymer of chloroprene with vinyl butyrate	95	—44.5
Copolymer of chloroprene with vinyl propionate	95	—40.2
Copolymer of chloroprene with vinyl acetate	95	—44.2

b) Solubility of copolymers of chloroprene with other esters. Copolymers of chloroprene with vinyl acetate containing 80-98 moles % of chloroprene are soluble in benzene, toluene, and pyridine, are insoluble in methanol, ethanol, and diethyl ether, and are partially soluble in acetone. Copolymers of chloroprene with vinyl propionate containing 89-96 moles % of chloroprene are soluble in benzene, pyridine, and dioxan and insoluble in methanol, ethanol, and acetone. Copolymers of chloroprene with vinyl butyrate containing 88-98 moles % of chloroprene are soluble in benzene, pyridine, and dioxan and insoluble in acetone, methanol, and ethanol. Copolymers containing 50-60 moles % of chloroprene are already soluble in alcohols, ether, and acetone. Thus, all the copolymers are soluble in organic solvents and, as the vinyl ester content of the copolymer increases, its solubility in nonpolar solvents diminishes and its solubility in polar solvents increases.

c) Intrinsic viscosity of copolymers. As is well known, for the determination of the molecular weights of high polymers from their intrinsic viscosities an equation of the form

$$[\eta] = KM^{\alpha}. \tag{4}$$

has been proposed [15].

Although K and α are unknown for our copolymers, a knowledge of the intrinsic viscosities enables us to compare and characterize our samples of copolymers to a certain extent. The intrinsic viscosities of the copolymers were determined by graphical extrapolation from the experimentally found values of η_{sp}/C for various concentrations in chloroform solution (in benzene solution in one case only). Specific viscosities were determined in a closed Ostwald viscometer at 20°. The concentration of the solution was expressed in g/100 ml. Like that of polychloroprene prepared under similar conditions, the intrinsic viscosities of the copolymers were low and varied very little with change in composition over the range studied; they varied from 0.2 to 0.35.

d) Glass points of copolymers. The glass point is a very important characteristic of a polymer, since it characterizes its stability to frost and its elasticity under conditions of use. The glass point depends both on the mobility of sections of the chains and on the potential barrier of the molecule itself, which, in its turn is determined both by intra- and intermolecular interactions. For most of the samples the glass point was determined mechanically in Marei's apparatus [16]. For some samples it was determined dilatometrically in a mercury dilatometer [17].

The results show that the introduction of a vinyl ester into the polychloroprene chain in amounts to 5-30 moles % does not raise the glass point appreciably.

SUMMARY

1. Conditions were found for the preparation of the previously undescribed copolymers of chloroprene with vinyl formate, vinyl acetate, vinyl propionate, and vinyl butyrate.

2. The copolymerization constants r_1 and r_2 were determined for vinyl formate, vinyl acetate, vinyl propionate, and vinyl butyrate in reaction with chloroprene at 65° with the aid of the method of the "selected curve."

3. Relative activities with respect to the chloroprene radical were calculated for these vinyl esters.

4. Integral and differential compositions were calculated for copolymers of chloroprene with vinyl formate.

5. Some of the properties of the copolymers were determined.

LITERATURE CITED

[1] K. W. Doak, and L. Dieneen, J. Am. Chem. Soc. 73, 1084 (1951); F. T. Wall, J. Pol. Sci. 2, 542 (1947); T. Alfrey, A. J. Goldfinger, and W. P. Hohenstein, J. Am. Chem. Soc. 68, 2464 (1946); F. C. Foster, J. Pol. Sci. 5, 369 (1950).

[2] G. A. Shtraikhman, Candidate's Thesis, Leningrad Technological Institute, 1950.

[3] W. H. Carothers, J. Williams, A. M. Collins, and J. F. Kirby, J. Am. Chem. Soc. 53, 4203 (1931).

[4] S. N. Ushakov, I. A. Arbuzova, and E. N. Rostovsky, J. Appl. Chem. 20, 1013 (1947).

[5] C. E. Schildknecht, Vinyl and Related Polymers, N. Y., London, 1952.

[6] E. N. Rostovsky, J. Appl. Chem. 1101 (1954).

[7] M. O. Korshun and N. E. Gelman, New Methods of Elementary Microanalysis, Goskhimizdat, Moscow and Leningrad, 1949, p. 77. *

[8] F. R. Mayo, and F. M. Lewis, J. Am. Chem. Soc. 66, 1594 (1944).

[9] T. Alfrey, J. Bohrer, and H. Mark, Copolymerization (Translated from English), Foreign Lit. Press, Moscow, 1953, p. 17.

[10] P. Argon, T. Alfrey, J. Bohrer, H. Haas, and H. Wechsler, J. Pol. Sci. 3, 157 (1948).

[11] E. C. Chapin, G. E. Ham, and C. L. Mills, J. Pol. Sci. 4, 597 (1949).

[12] S. N. Ushakov and A. F. Nikolaev, Bull. Acad. Sci. USSR, Div. Chem. Sci. USSR, 1956,** 83.

* In Russian.

** Original Russian pagination. See C. B. Translation.

[13] S. S. Medvedev, A. D. Abkin, and L. M. Gindin, J. Phys. Chem. 11, 1269 (1947).

[14] S. N. Ushakov, S. P. Mitsengendler, and B. M. Polyatskina, J. Appl. Chem. 23, 521 (1950).

[15] A. A. Tager, Solutions of Macromolecular Compounds, Goskhimizdat, Moscow, 1951.*

[16] A. I. Marei, Investigations on Synthetic Rubber, No. III, Trans. Lebedev All-Union Research Inst. Synthetic Rubber, 1951, p. 173. *

[17] S. N. Ushakov and T. A. Kononova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, 335.**

Institute of Macromolecular Compounds of
the Academy of Sciences of the USSR

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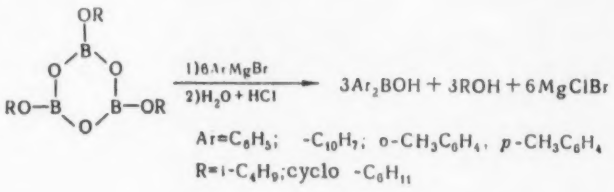
BRIEF COMMUNICATIONS

ORGANOBORON COMPOUNDS

COMMUNICATION 18. NEW METHOD OF SYNTHESIS OF DIARYLBORINIC ACIDS

B. M. Mikhailov and V. A. Vaver

Reaction between arylmagnesium halides and orthoboric esters at low temperatures (from -70° to -75°) gives diarylborinic esters [1, 2], which may be isolated as such or may be converted into the corresponding 2-aminoethyl esters [3, 4]. We found that organomagnesium compounds react also with metaboric esters, but in this case, instead of diarylborinic esters, diarylborinic acids are formed:



Ar = C_6H_5; $-C_{10}H_7$; o-$CH_3C_6H_4$, p-$CH_3C_6H_4$

R = i-C_4H_9; cyclo-C_6H_{11}

This method is a convenient simple method for preparing diarylborinic acids (and their esters), long periods at low temperatures being unnecessary. It is more general than the method of synthesis based on trialkyl borates: by the latter method satisfactory yields were not obtained of, for example, di-o-tolyl- and di-p-tolyl-borinic acids (the yields did not exceed 7-15%), whereas the method now described gives these esters in yields of 40-42%. By the action of phenylmagnesium bromide on isobutyl metaborate we obtained diphenylborinic acid, which we isolated as its anhydride. Di-1-naphthylborinic acid was also obtained in good yield.

EXPERIMENTAL

Diphenylborinic Anhydride. A benzene solution of 9.0 g (0.03 mole) of isobutyl metaborate* was added to an uncooled vigorously stirred solution of 0.2 mole of phenylmagnesium bromide. When evolution of heat ceased, the reaction solution was boiled for one hour and then hydrolyzed with 200 ml of 3.5% of hydrochloric acid. The ether layer was rapidly separated, and the solution was extracted with ether. In order to remove solvents and isobutyl alcohol under conditions precluding esterification, we used an apparatus consisting of a two-necked pear-shaped flask fitted with a capillary connected with a condenser set for distillation through a Claisen stillhead. The apparatus was evacuated and the flask was placed in a water bath at 35-40°, after which the ethereal solution of hydrolysis products of the reaction mixture was added through a capillary funnel, the solution being added at about the same rate as that at which solvents and alcohol were removed. The latter were trapped completely in a receiver cooled to -75° with a mixture of solid carbon dioxide and acetone. In the course of 20-30 minutes the removal of volatile substances and traces of water was complete. The contents of the flask were held for 15-20 minutes at 90° (8 mm), cooled, and diluted with a mixture of 20 ml of hexane and 10 ml of absolute ether. The small precipitate formed in the dilution was filtered off, washed with hexane, and vacuum-dried. This product was benzeneboronic anhydride, m.p. 190-193°, amounting to 0.77 g (8.3%). Hexane and ether were removed, and the residue was diluted with 25 ml of isopentane. Colorless crystalline diphenylborinic anhydride was filtered off, washed with isopentane, and vacuum-dried; yield 8.10 g (51.6%); m.p. 123-125°. After being recrystallized once from a 1:10 mixture of benzene and isopentane,

*This was synthesized in the same way as butyl metaborate [5] and used in the form of the benzene solution obtained directly in the esterification.

the anhydride melted at 130-131°. The mixture of ether and isobutyl alcohol was dried with anhydrous copper sulfate, and ether was driven off through a small column. The residue gave 6.1 ml of isobutyl alcohol, b.p. 104-107° (760 mm). In the aqueous solution obtained after treatment of the reaction mixture with hydrochloric acid and separation of the ether layer, titration in presence of mannitol gave a content of 1.39 g (25.8%) of boric acid.

2-Aminoethyl Diphenylborinate. A solution of 6.0 g (0.0163 mole) of cyclohexyl metaborate, m.p. 162-164° [5], in 30 ml of benzene was added to an ethereal solution of 0.1 mole of phenylmagnesium bromide. After being boiled for two hours, the solution was hydrolyzed with 100 ml of 3.5% hydrochloric acid. In the aqueous solution 29.4% of boric acid was found. The residue remaining after removal of solvents from the ether-benzene solution of the reaction products was diluted with 30 ml of 60% ethanol and mixed with 5.0 ml of 2-aminoethanol. This gave 6.22 g (62%) of 2-aminoethyl diphenylborinate, m.p. 186-188°. After being recrystallized from alcohol the 2-aminoethyl ester melted at 190-191° [4].

Di-1-naphthylborinic Acid. Reaction was between 0.1 mole of 1-naphthylmagnesium bromide and 0.015 mole of isobutyl metaborate. A benzene solution of the metaboric ester was added to a suspension of the 1-naphthylmagnesium bromide in 100 ml of dry ether. The organomagnesium compound dissolved rapidly and the solution came to the boil. When spontaneous evolution of heat ceased, the solution was boiled for one hour and was treated with 100 ml of 3.5% hydrochloric acid. The organic layer was separated, solvent was removed under the same conditions as in the synthesis of diphenylborinic anhydride, and the residue was diluted with 25 ml of isopentane. The di-1-naphthylborinic acid was recrystallized from a 1:5 mixture of benzene and hexane; yield 9.7 g (76.6%) m.p. 114-115° [2]. In the aqueous solution 7.3% of boric acid was found.

2-Aminoethyl Di-p-tolylborinate. Reaction between 0.4 mole of p-tolylmagnesium bromide and 0.0514 mole of isobutyl metaborate was carried out under the conditions described above. After removal of solvents, the mixture of reaction products was diluted with 60% ethanol and treated with 9 ml of 2-aminoethanol. The product, amounting to 16.10 g (41%), was 2-aminoethyl di-p-tolylborinate, m.p. 170-173°. It crystallized from alcohol in the form of leaves, m.p. 174.5-176°.

Found %: C 76.11; H 7.90; B 4.33; N 5.56. $C_{16}H_{20}BON$. Calculated %: C 75.91; H 7.96; B 4.27; N 5.53.

The filtrate from the 2-aminoethyl ester was acidified with 3.5% hydrochloric acid, and the organic layer was extracted with ether. After removal of solvent, the residue was esterified with 20 ml of isobutyl alcohol and vacuum fractionated; this gave 11.16 g (21.2%) of diisobutyl p-toluenebornate; b.p. 127-128° (5.5 mm) d_4^{20} 0.9106; n_D^{20} 1.4761.

Found %: $CH_3C_6H_4$ 36.64; B 4.34. $CH_3C_6H_4(OC_4H_9)_2$. Calculated %: $CH_3C_6H_4$ 36.72; B 4.36.

This is a colorless liquid, miscible in all proportions with organic solvents, and hydrolyzed in the air. In the aqueous solution 20.4% of boric acid was found.

Isobutyl Di-o-tolylborinate. Reaction as above between 0.2 mole of o-tolylmagnesium bromide and 0.03 mole of isobutyl metaborate gave, after hydrolysis of the reaction mixture, esterification of the reaction products with isobutyl alcohol, and vacuum fractionation, 4.74 g 111-115° (3 mm);

Found %: $CH_3C_6H_4$ 36.67; B 4.30. $CH_3C_6H_4B(OC_4H_9)_2$. Calculated %: $CH_3C_6H_4$. 36.72; B 4.36.

and 10.02 g (42.0%) of isobutyl di-o-tolylborinate, b.p.151-153° 2.5 mm); d_4^{20} 0.9701, n_D^{20} 1.5432.

Found %: $CH_3C_6H_4$ 68.24; B 4.00. $(CH_3C_6H_4)_2BOC_4H_9$. Calculated %: $CH_3C_6H_4$ 68.47; B 4.06.

The di-o-tolylborinic ester is a colorless viscous liquid, miscible in all proportions with most organic solvents and slowly oxidized in the air.

All operations in which diarylborinic acids and their derivatives (except the 2-aminoethyl esters) were heated were carried out in an atmosphere of nitrogen.

SUMMARY

Treatment of metaboric esters with arylmagnesium halides gives diarylborinic esters. The method described makes it possible to prepare both diarylborinic acids and their esters in good yield.

LITERATURE CITED

[1] B. M. Mikhailov and V. A. Vaver, Proc. Acad. Sci. USSR 102, 531 (1955).*

[2] B. M. Mikhailov and V. A. Vaver, Bull. Acad. Sci. USSR, Div. Chem. Soc. 1956,*

[3] R. Letsinger, and N. Remes, J. Am. Chem. Soc. 77, 2489 (1955).

[4] R. Letsinger, and J. Skoog, J. Am. Chem. Soc. 77, 2491 (1955).

[5] G. L. O'Connor, and H. R. Nace, J. Am. Chem. Soc. 77, 1578 (1955).

N. D. Zelinsky Institute of Organic Chemistry
of the Academy of Sciences of the USSR

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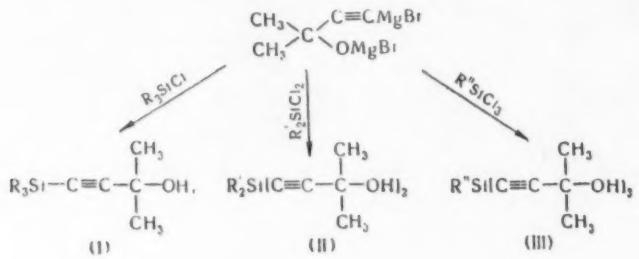
SYNTHESIS AND REACTIONS OF UNSATURATED ORGANOSILICON COMPOUNDS

COMMUNICATION 5. SYNTHESIS OF MIXED DIACETYLENIC ORGANOSILICON GLYCOLS

I. A. Shikhiev and L. A. Kayutenko

The reactivities of tertiary acetylenic alcohols and their derivatives have been studied thoroughly over a long period by the Favorsky school [1]. In our previous investigations [2-4] we showed that in the reaction of mono-, di-, and even tri-alkylchlorosilanes with the bisbromomagnesium derivative of 2-methyl-3-butyn-2-ol the corresponding acetylenic alcohols are formed as follows:

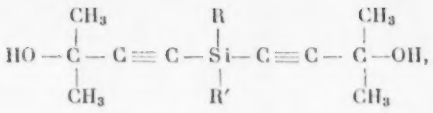


There are no other data in the literature on the reaction of mono- and di-alkylchlorosilanes with the bisbromomagnesium derivative of 2-methyl-3-butyn-2-ol. Only one paper [5] has appeared on reaction between trialkylchlorosilanes and the bisbromomagnesium derivative of 2-methyl-3-butyn-2-ol, and this contains experimental data in accord with reaction by the following scheme:

(IV)

The authors of this paper expected the formation of an alcohol and therefore tried to dehydrate their products with iodine, but they found no signs of dehydration. The authors showed by spectroscopic analysis that the compound (IV) did indeed correspond in structure to the compound indicated as such above. On this basis the authors [5] concluded that in the reaction between these substances only the compound (IV) is formed.

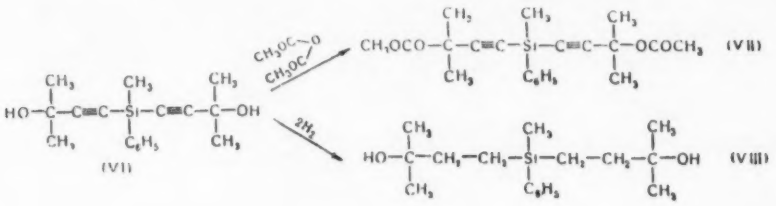
However, our investigations [3] established that in the reaction between trialkylchlorosilanes and the bisbromomagnesium derivative of 2-methyl-3-butyn-2-ol the corresponding acetylenic alcohols (I) are formed and the formation of (IV) is not observed. As we were interested in alcohols of the structure indicated, we continued their synthesis by our proposed method. The object of the present investigation was the synthesis of the following mixed diacetylenic organosilicon glycols:



(V)

in which R = CH_3, C_2H_5, C_6H_5; R' = C_6H_5, $C_{10}H_7$.

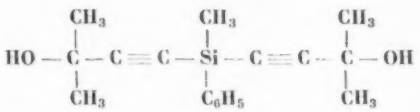
The structure of the mixed diacetylenic organosilicon glycols was proved by their acetylation and hydrogenation:



The synthesis of compounds (V) – (VIII) indicates convincingly that their formation is in complete accord with the schemes (I) – (III) that we have established. At the same time this permits us to conclude that Petrov and Shchukovskaya erroneously assumed the formation of the compounds (IV) instead of the acetylenic alcohols (I) (III) actually obtained.

EXPERIMENTAL

1. Synthesis of 4,4'-(Methylphenylsilylene)bis[2-methyl-3-butyn-2-ol]



(VI)

A solution of 0.5 mole of 2-methyl-3-butyn-2-ol in 50 ml of dry ether was added with constant stirring and cooling with ice water to 1 mole of Grignard reagent. Stirring and cooling with ice water was continued for two hours, and 0.25 mole (48 g) of dichloromethylphenylsilane was then added dropwise. The reaction mixture was heated for four hours. On the next day the thick complex was decomposed with 10-15% hydrochloric acid, cooling being applied. The aqueous and ethereal layers were separated, and the latter was dried with sodium sulfate; ether was distilled off. Three crystallizations of the residue from dry benzene gave white crystals, m.p. 129-130°; yield 34.0 g (47.4% on the 2-methyl-3-butyn-2-ol taken).

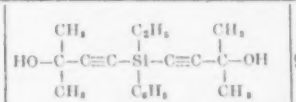
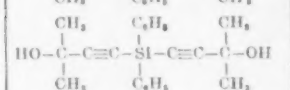
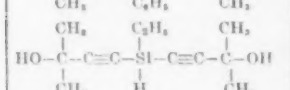
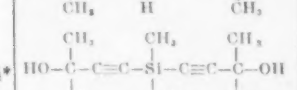
Found %: C 71.43; H 7.61; Si 9.58. $C_{27}H_{22}SiO_2$. Calculated %: C 71.98; H 7.74; Si 9.81.

The results correspond to the diacetylenic glycol (VI).

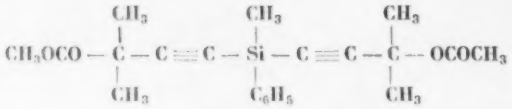
In a similar way we prepared four other organosilicon glycols, analytical data for which are given in the table.

TABLE

General Characterization of Organosilicon Diacetylenic Glycols

No.	Formula of glycol	M. p. (°C)	found g %			calculated g %			Yield %
			C	Si	H	C	Si	H	
1		92—93	71.69 71.75	9.33 8.95	8.09 8.06	71.95	9.35	8.05	57.3
2		123—124	75.76 75.91	7.79 8.00	7.04 6.92	75.82	8.05	6.93	43.7
3		62—63	63.77 63.60	12.93 12.66	8.97 9.00	64.23	12.52	8.99	83.8
4*		92—93	75.05 74.98	8.16 8.35	7.28 7.19				56.5

2. Synthesis of 4,4'-(Methylphenylsilylene)bis[2-methyl-3-butyn-2-ol] Diacetic Ester



(VII)

Acetic anhydride (100 ml) was added to 14.3 g (0.05 mole) of 4,4'-(methylphenylsilylene)bis[2-methyl-3-butyn-2-ol] contained in a three-necked flask. The reaction mixture was heated in a boiling water bath for 13 hours. Acetic acid and unchanged acetic anhydride were then distilled off. Vacuum fractionation of the residue gave a main fraction of b.p. 178-179° (4 mm) in 68% yield; d_4^{20} 1.0281; n_D^{20} 1.5112; found MR 106.20; calculated MR 105.98.

Found %: C 68.90; H 7.11; Si 7.29. Calculated %: C 68.07; H 7.07; Si 7.58.

The analytical data correspond to the diacetic ester (VII).

Hydrolysis of the diacetic ester with 0.1 N NaOH gave a crystalline substance of m.p. 128°, undepressed by admixture of the original glycol (VI).

3. Quantitative Catalytic Hydrogenation of 4,4'-(Methylphenylsilylene)bis[2-methyl-3-butyn-2-ol]

A mixture of 1 g of Raney nickel and 50 ml of ethanol was prepared in a hydrogenation flask, and hydrogen was passed with constant shaking. The glycol (3 g, i.e., 0.01 mole) was then introduced into the flask. Hydrogenation was slow; 960 ml of hydrogen was absorbed at 0° and 760 mm (theory requires 900 ml at 0° and 760 mm). Catalyst was then filtered off; the alcohol was evaporated, and the product crystallized out. Recrystallization from benzene gave white crystals of m.p. 93-94°. The number of active hydrogens in the completely hydrogenated glycol was found to be 1.86 (theory requires two). The analytical results showed that the hydroxy groups of the glycol were not replaced by hydrogen. The completely hydrogenated glycol did not decolorize bromine water.

* 4,4'-(Methylnaphthylsilylene)bis[2-methyl-3-butyn-2-ol] was prepared in collaboration with Kh. I. Kondratyev.

SUMMARY

1. A method was developed for the preparation of mixed diacetylenic organosilicon glycols. Five such glycols were prepared for the first time: 4,4'-(methylphenylsilylene)-, 4,4'-(ethylphenylsilylene)-, 4,4'-(diphenylsilylene)-, 4,4'-(diethylsilylene)-, and 4,4'-(methylnaphthylsilylene)-bis[2-methyl-3-butyn-2-ol].

2. The presence of hydroxy groups in the mixed organosilicon glycols was proved by the synthesis of the corresponding acetyl derivatives (VI).

3. 4,4'-(Methylphenylsilylene)bis[2-methyl-3-butyn-2-ol] diacetic ester and 4,4'-(methylphenylsilylene)-bis[2-methyl-2-butanol] were prepared and characterized for the first time.

4. The presence of two triple bonds in the glycols was proved by quantitative catalytic hydrogenation to the corresponding saturated compounds.

LITERATURE CITED

[1] A. E. Favorsky, Soviet Patent No. 31016 to 11. VII. 1932; A. E. Favorsky, Selected Works, Moscow, 1940; T. A. Favorsky et al., J. Gen, Chem. 10, 461, 451, 446 (1940); I. N. Nazarov, Prog. Chem. 20, 309 (1951); S. N. Danilov, J. Gen. Chem. 10, 587 (1940); I. A. Shikhiev, J. Gen. Chem. 16, 657 (1946); 20, 839 (1950);* M. F. Shostakovsky and I. A. Shikhiev, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1953,* 106; 1954,* 931, 945.

[2] M. F. Shostakovsky, I. A. Shikhiev, and N. V. Komarov, Proc. Acad. Sci. USSR 109, 344 (1956).*

[3] I. A. Shikhiev, M. F. Shostakovsky, and N. V. Komarov, Proc. Azerbaizhan Acad. Sci. 12, 553 (1956).

[4] M. F. Shostakovsky, I. A. Shikhiev, and N. V. Komarov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1956,* 1271.

[5] A. D. Petrov, L. L. Shchukovskaya, and Yu. P. Egorov, Proc. Acad. Sci. USSR 93, No. 2, 293 (1953).

N. D. Zelinsky Institute of Organic Chemistry
of the Academy of Sciences of the USSR

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DIRECT SYNTHESIS OF HALOMETHYLGERMANES, AND THEIR HALOGEN-EXCHANGE AND PHOTOCHEMICAL-CHLORINATION REACTIONS

V. A. Ponomarenko and G. Ya. Vzenkova

In 1947 Rochow [1] showed the possibility of preparing halomethylgermanes by direct synthesis from germanium in presence of copper at 340-460°. In preparations by this method we found that, both with CH_3Cl and with CH_3Br, the relative amounts of the compounds $(CH_3)_2GeX_2$ (I) and CH_3GeX_3 (II) formed at a given temperature are greatly dependent on the copper content of the mixture or alloy of germanium and copper: Particularly in the case of bomomethylgermanes, the relative yield of (II) is the greater, the greater the amount of copper used. Thus, whereas the bromomethylgermanes (I) and (II) were obtained in the proportions 1:2.5 from a 1:1 germanium-copper alloy, they were obtained in the proportions 1:0.7 from a 4:1 germanium-copper mixture. The proportions of (I) and (II) vary in the course of a given experiment. For the chloromethylgermanes obtained in one experiment (Ge:Cu = 4:1) the proportions were 4.5:1 at the beginning of the reaction, 2.4:1 in the middle, and 1.4:1 at the end. In the case of bromomethylgermanes, as the relative amount of copper increases during reaction, the ratio of the amounts of (I) and (II) moves still more sharply in the direction of (II): in some experiments we observed the formation of only (II). Like Rochow, in the direct synthesis we did not observe the formation of $(CH_3)_3GeCl$, which was described by Rochow in another paper [2].

We repeated this work [2] and found that Rochow's conclusions regarding the properties of $(CH_3)_3GeCl$ were incorrect. We prepared $(CH_3)_3GeCl$ from $(CH_3)_2GeCl_2$ and CH_3MgBr. In the further investigation of the products of this reaction we succeeded in isolating dibromodimethylgermane in 25% yield. The unexpected formation of this can be explained by the reaction $(CH_3)_2GeCl_2 + 2MgClBr \rightarrow (CH_3)_2GeBr_2 + 2MgCl_2$. The correctness of this reaction scheme was confirmed by the preparation of $(CH_3)_3GeBr$ from $(CH_3)_3GeCl$ and MgClBr.

A similar reaction of organosilicon compounds was observed by us in the case of the preparation of compounds of the type RR'SiHCl from $RSiHCl_2$ and R'MgBr [3]. Relevant in this connection is the observation of West and co-workers [4], who obtained $(CH_3)_3GeI$ instead of $(CH_3)_3GeOCH_3$ from $(CH_3)_2Ge(OCH_3)_2$ and CH_3MgI.

It is known [5] that the use of the double salt magnesium chloride iodide MgClI makes it possible to prepare many trialkyl(iodomethyl)silanes with relative ease. In the present investigation, taking $(CH_3)_3GeCH_2I$ as our example, we have confirmed the possibility of preparing analogous germanium compounds in the same way.

As would be expected, mono-, di-, and tri-chloro(or bromo)germanes can be caused to exchange their chlorine or bromine for fluorine with the aid of SbF_3.

We prepared the above-mentioned $(CH_3)_3GeCH_2I$ from $CH_3GeCl_2(CH_2Cl)$, which was first synthesized by the diazo method [6]. For the preparation of the latter we used the method of photochemical chlorination with removal of the chlorinated products from the reaction zone, which has been worked out in detail for organosilicon compounds [5, 7]. The yield of $CH_3GeCl_2(CH_2Cl)$ from $(CH_3)_2GeCl_2$ was fairly high, but was lower than that of $CH_3SiCl_2(CH_2Cl)$ in the chlorination of $(CH_3)_2SiCl_2$. The same occurs also in the chlorination of trichloromethylgermane. We isolated Cl_3CGeCl_3 in considerable amounts. These facts are interesting in that, as Petrov, Mironov, and Dolgy [8] showed recently, sulfuryl chloride in presence of benzoyl peroxide does not chlorinate CH_3GeCl_3, but does chlorinate C_2H_5GeCl.

EXPERIMENTAL

1. $(CH_3)_2GeBr_2$ (I) and CH_3GeBr_3 (II) were prepared by direct synthesis from CH_3Br and 400 g of Ge (5 experiments) at 450° in presence of copper (Ge : Cu = 4 : 1). The amount of (I) obtained was 283 g; b.p. 153° (746 mm); d_4^{20} 2.1163; n_D^{20} 1.5268; found MR 38.12; calculated MR 38.44.

Found %: C 9.37, 9.37; H 2.66, 2.57; Ge 28.05, 28.28; Br 60.46, 60.31. $(CH_3)_2GeBr_2$. Calculated %: C 9.15; H 2.30; Ge 27.66; Br 60.88.

The amount of (II) isolated was 331 g; b.p. 168° (750 mm); d_4^{20} 2.6337; n_D^{20} 1.5770; MR 41.19; calculated MR 41.42.

Found %: C 3.94, 3.92; H 1.23, 1.15; Ge 23.85, 24.68; Br 72.54, 71.82. CH_3GeBr_3. Calculated %: C 3.66; H 0.92; Ge 22.25; Br 73.17.

2. $(CH_3)_3GeCl$ (III) and also (I) were obtained from 740 g of $(CH_3)_2GeCl_2$ and CH_3MgBr (8 experiments). The amount of (III) isolated was 75 g (12%); b.p. 98° (736 mm); d_4^{20} 1.2493; n_D^{20} 1.4337; found MR 31.91; calculated MR 31.96.

Found %: C 23.65, 23.83; H 6.00, 5.80; Ge 47.68, 48.28; Cl 21.92, 20.61. $(CH_3)_3GeCl$. Calculated %: C 23.53; H 5.88; Ge 47.71; Cl 22.88.

The amount of (I) isolated was 267 g (25%); b.p. 152.3° (755 mm); d_4^{20} 2.1182; n_D^{20} 1.5265; found MR 38.08; calculated MR 38.44.

Found %: C 9.06, 9.23; H 2.20, 2.30; Ge 27.88, 27.41; Br 60.86, 61.04. $(CH_3)_2GeBr_2$. Calculated %: C 9.15; H 2.30; Ge 27.66; Br 60.89.

3. $(CH_3)_3GeBr$ was prepared in a yield of 6.2 g (22%) from 21.5 g (III) and MgClBr in 200 ml of ether with subsequent heating in a boiling water bath for 10 hours; b.p. 115° (755 mm); d_4^{20} 1.5486; n_D^{20} 1.4660; found MR 35.34; calculated MR 35.46.

Found %: C 18.58, 18.30; H 4.68; 4.77. $(CH_3)_3GeBr$. Calculated %: C 18.28; H 4.60.

4. $(CH_3)_3GeCH_2I$ (IV) was obtained in a yield of 12 g (24%) from 41 g of $CH_3GeCl_2(CH_2Cl)$ and CH_3MgI prepared from 10 g of Mg and 62 g of CH_3I in 200 ml of ether under conditions described in [5].

(IV) had the following constants: b.p. 154° (752 mm); d_4^{20} 1.7160; n_D^{20} 1.5112; found MR 45.17; calculated MR 45.34.

Found %: C 18.71, 18.81; H 4.32, 4.59. $(CH_3)_3GeCH_2I$. Calculated %: C 18.61; H 4.30.

5. Cl_3GeCH_2Cl (V) was prepared in a yield of 24 g (18.5%) from 131 g of Cl_3GeCH_3 (VI) under the conditions described in [5], and it had the following properties: b.p. 149° (759 mm); d_4^{20} 1.8415; n_D^{20} 1.5003; found MR 36.51; calculated MR 35.78.

Found %: C 5.14, 5.39; H 0.82, 0.91. Cl_3GeCH_2Cl. Calculated %: C 5.26; H 0.88.

The residue (35 g) contained a considerable amount of di- and tri-chloro compounds. Some (VI) (21 g) was recovered unchanged.

6. Cl_3GeCCl_3 was obtained in a yield of 17 g by chlorination of 51 g of (VI) under the same conditions; b.p. 130° (200 mm) and m.p. 106-107°.

Found %: C 4.45, 4.66. Cl_3GeCCl_3. Calculated %: C 4.05.

7. $CH_3GeCl_2(CH_2Cl)$ (VII) was prepared in a yield of 73.5 g (3 experiments) from 193 g of $(CH_3)_2GeCl_2$ (VIII) under the conditions described above. The maximum yield on the amount of (VIII) that reacted was 51%. The constants of (VII) were b.p. 155° (750 mm); d_4^{20} 1.6694; n_D^{20} 1.4930; found MR 36.22; calculated MR 36.28.

Found %: C 11.05, 11.00; H 2.39, 2.36; Ge 34.42, 34.46; Cl 50.96, 51.24. $CH_3GeCl_2CH_2Cl$. Calculated %: C 11.55; H 2.42; Ge 34.90; Cl 51.13.

The residue contained a small amount of more highly chlorinated products.

8. $(CH_3)_3GeF$ [b.p. 76° (746 mm); d_4^{20} 1.2300; n_D^{20} 1.3863], $(CH_3)_2GeF_2$ [b.p. 112° (750 mm); d_4^{20} 1.5726; n_D^{20} 1.3743] and CH_3GeF_3 [b.p. 96.5° (751 mm); b.p. 38°] were prepared by the Swarts reaction from the corresponding chloro and bromo compounds.

SUMMARY

1. It is pointed out that the relative amounts of halomethyl- and halodimethylgermanes obtained in their direct synthesis from germanium and CH_3X are greatly affected by the amount of copper used.

2. It is shown that Rochow's conclusions regarding the properties of chlorotrimethylgermane are incorrect.

3. It is shown that it is possible to prepare dibromodimethylgermane, bromotrimethylgermane, and trialkyl(iodomethyl)germanes from the corresponding chloro compounds by exchange reactions with MgClBr and MgClI.

4. It is shown that chloro(chloromethyl)germanes can be prepared by the photochemical chlorination of organogermanium compounds with application of the principle of removal of reaction products from the chlorination zone.

LITERATURE CITED

[1] E. G. Rochow, J. Am. Chem. Soc. 69, 1729 (1947).

[2] E. G. Rochow, J. Am. Chem. Soc. 70, 436 (1948).

[3] A. D. Petrov, V. A. Ponomarenko, B. A. Sokolov, and G. V. Odabashyan, Bull. Acad. Sci. USSR, Div. Chem. Sic. 1947 (in the press).

[4] R. West, H. Hunt, and R. O. Whipple, J. Am. Chem. Soc. 76, 310 (1954).

[5] V. A. Ponomarenko and V. F. Mirohov, Proc. Acad. Sci. USSR 94, No. 3, 485 (1954).

[6] D. Seyferth, and E. G. Rochow, J. Am. Chem. Soc. 77, 907 (1955).

[7] V. F. Mironov and V. A. Ponomarenko, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1957,* 199.

[8] A. D. Petrov, V. F. Mironov, and I. E. Dolgy, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1956,* 1146.

P. N. Lebedev Physical Institute of
the Academy of Sciences of the USSR
and
N. D. Zelinsky Institute of Organic Chemistry
of the Academy of Sciences of the USSR

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MODIFICATION OF THE PROTEIN MOLECULE

COMMUNICATION 1. REACTION OF PRIMARY DEGRADATION PRODUCTS OF PROTEINS WITH ANHYDRIDES OF N-CARBOXY-GLYCINE, -DL-ALANINE, AND -DL-PROLINE

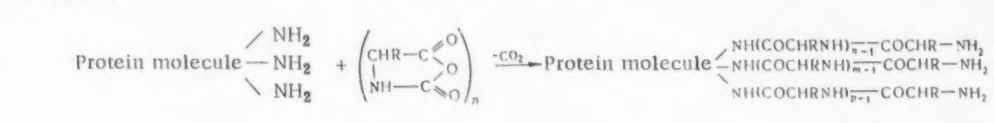
K. T. Poroshin

Great importance is to be attached not only to the synthesis of the protein molecule, but also to synthetic methods leading to the modification of the physical, physicochemical, and biological properties of proteins. One of the principal methods of modifying the chemical composition of a protein is based on the introduction of other amino acids into its molecule, combination being effected via peptide linkages.

Lisitsyn and Aleksandrovskaya [1] synthesized protamine derivatives having branched chains by the introduction of various amino acids into the molecule with formation of additional peptide linkages; they succeeded in uniting one amino acid residue to each free amino group.

Becker and Stahmann [2] investigated the reaction of various anhydrides of carboxyamino acids with albumins in buffer solutions. Sela and Katchalski [3] introduced polytyrosine into the composition of gelatin, thus increasing the tyrosine content of the gelatin to 16%; the gelatin then acquired the ability to bring about anaphylactic shock. Tsuyuki, Van Kley, and Stahmann [4] modified the albumin molecule by copolymerizing it with the anhydrides of N-carboxylysine and glutamic acid.

In the present paper we describe experiments on the reaction of anhydrides of N-carboxy-glycine, -DL-alanine, and -DL-proline with primary degradation products of casein – the peptone hydrolyzate. We consider that the reaction initiators in the copolymerization or copolycondensation of an anhydride of an α-(carboxyamino) acid with a peptone hydrolyzate may be the α-amino groups of the peptides $H(HN-CHR-CO)_nOH$, the ε-amino group of lysine present in the peptide chain, and also amidine and guanidine groupings. The general scheme of reaction between α-(carboxyamino) acids and a peptone hydrolyzate may be represented as follows:

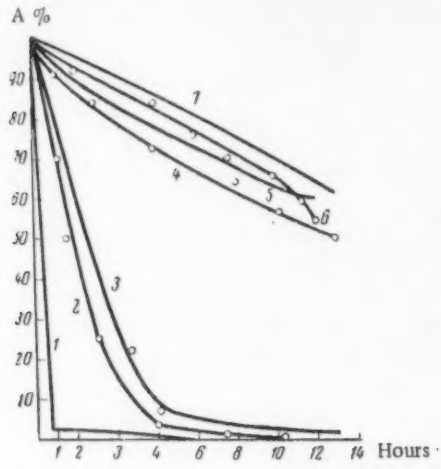


The experiments on the reaction of anhydrides of α-(carboxyamino) acids with the peptone hydrolyzate of casein were preceded by investigations on the action of various initiators on the anhydrides.

EXPERIMENTAL

1. Initiation of Action of Anhydrides of α-(Carboxyamino) Acids. With the object of studying the action of various initiators on anhydrides of α-(carboxyamino) acids (derived from glycine and DL-alanine), we took the following initiators: $NH_2-CH_2COOC_2H_5$; $NH_2-CO-NHCH_2COOC_2H_5$; $NH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CO-NHCH_2-CO-NH-CH_2COOCH_3$; peptone hydrolyzate of casein; the ethyl ester of a polyglycine having $\underline{n} = 8\text{-}10$; water; casein. The initiator (I) was added to 10-mg portions of the α-(carboxyamino) acid anhydride (A), A/I ratios

of 0.1, 25, and 50 being used. The solution was then placed in a thermostat at 40°, and at definite intervals the unchanged anhydride was determined by the method of Berger, Sela, and Katchalski [5]. The results are shown in the figure, from which it can be seen that the initiators can be divided into two groups according to the character of their action. The first group includes amines taken in the form of esters of amino acids and peptides. Initiators of the first group are more active than those of the second. The tendency for glycine ethyl ester to act as an initiator is particularly notable (Curve 1). The peptone hydrolyzate of casein (Curve 4), which can be regarded as a multivalent amine initiator, is the most effective of the second group.



Initiation of action of anhydrides of α-(carboxyamino) acids: 1) glycine ethyl ester; 2) diglycine ethyl ester; 3) alanylglycylglycine methyl ester; 4) casein peptone hydrolyzate; 5) polyglycine ethyl ester; 6) water; 7) casein.

2. Reaction of Anhydrides of α-(Carboxyamino) Acids with Casein Peptone Hydrolyzates. The casein peptone hydrolyzates were prepared by a method described previously [6]. The preparations had the following characteristics: total nitrogen 14.55%; amine nitrogen 1.75%; arginine 4.8%; lysine 14.8% (according to Khurgin's results); molecular weight 750. Both the fractions that readily diffused through Cellophane and also the fractions not salted out by sodium chloride were taken for the experiments. The peptone hydrolyzate was prepared from casein prepared in the form of a casein acid by Perov's method [7]. This protein preparation had the following characteristics: titer 8.35; total nitrogen 15.60; amine nitrogen 0.32%; arginine 4.45%; lysine 10.5% (according to Khurgin's results); molecular weight 412,000.

The procedure in the copolymerization or copolycondensation of anhydrides of α-(carboxyamino) acids with the casein peptone hydrolyzate was as follows. A weighed amount of the α-(carboxyamino) acid anhydride was dissolved in dioxan , and a cooled aqueous solution of the peptone hydrolyzate was stirred in. The solution was then placed for one day in a cupboard maintained at 1-2°. Simultaneously several experiments were carried out with a phosphate buffer solution. At the end of the reaction time the solution was transferred to a vessel for dialysis through Cellophane. Fractions of low molecular weight were dialyzed away in the course of 5-6 days. The completion of dialysis was determined by biuret and ninhydrin tests, and sometimes also chromatographically on paper. Paper chromatography showed that only the low-molecular-weight fractions of the various poly (α-amino acids) passed into the dialyzed part. Chromatograms showed that, after hydrolysis with 6 N HCl, the undialyzed part contained the whole set of amino acids present in the original peptone hydrolyzate, but the contents of the amino acids brought into the reaction were greater. The whole of the peptone hydrolyzate that reacted with α-(carboxyamino) acid anhydride, owing to the increase in its molecular weight, lost its ability to dialyze through Cellophane. When we took the peptone hydrolyzate fraction that was not salted out with sodium chloride, then the "polypeptidylpeptone" formed by polycondensation was found to be salted out of solution by saturation with sodium chloride or ammonium sulfate.

It was found that 40-60% of α-(carboxyamino) acid anhydride reacted with the peptone hydrolyzate. For the polyglycylpeptone the degree of polymerization (n) of glycine was 8-10, and for poly-DL-alanylpeptone it was 18-20. By the procedure described we prepared the polyglycylpeptone of casein and the poly-DL-alanyl compound of the peptone hydrolyzate. Fractions of low molecular weight were removed from the latter, and the product was polycondensed with the anhydride of N-carboxy-DL-proline. The poly-DL-alaninepoly-DL-prolinepeptone of casein is readily soluble in water, is not dialyzed through Cellophane, and is readily salted out by sodium chloride and ammonium sulfate. Depending on the amount of N-carboxy-DL-proline taken, the amine-nitrogen content fell from 1.75% in the original material to 0.03%.

SUMMARY

1. The action of various initiators on the anhydrides of N-carboxyglycine and of N-carboxy-DL-alanine was studied.

2. Derivatives of casein were prepared, namely, polyglycyl, poly-DL-alanyl, and poly-DL-alanyl-DL-prolyl derivatives of its peptone hydrolyzate.

LITERATURE CITED

[1] M. A. Lisitsyn and N. A. Aleksandrovskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1941, 289.

[2] R. R. Becker, and M. A. Stahmann, J. Biol. Chem. 204, 737, 745 (1953).

[3] M. Sela, E. Katchalski, and A. Olitzi, Science 123, 1129 (1956).

[4] H. Tsuyuki, H. Van-Kley, and M. A. Stahmann, J. Am. Chem. Soc. 78, 764 (1956).

[5] A. Berger, M. Sela, and E. Katchalski, Anal. Chem. 25, 1554 (1953).

[6] S. S. Perov, Biochemistry of Proteins, Soviet Science Press, 1951,* p. 126; K. T. Poroshin, Trans. Lab. for Protein Studies of Acad. Sci. USSR, 1940, p. 133.*

[7] S. S. Perov, Biochemistry of Proteins, Soviet Science Press, 1951, p. 247.*

N. D. Zelinsky Institute of Organic Chemistry
of the Academy of Sciences of the USSR

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HETEROCHAIN POLYESTERS

COMMUNICATION 6. POLYESTERS OF 3,3'-METHYLENEDI-, 4,4'-METHYLENEDI-, AND 4,4'-CARBONYLDI-BENZOIC ACIDS

V. V. Korshak, S. V. Vinogradova, and V. M. Belyakov

In continuation of our study of the effect of the structures of the reacting components on the physical properties of the resulting polyesters we synthesized and investigated polyesters formed by 3,3'-methylenedi-, 4,4'-methylenedi-, and 4,4'-carbonyldi-benzoic acids with eleven aliphatic glycols of varied structure. Comparison of corresponding polyesters of 3,3'- and 4,4'-methylenedibenzoic acids data on which are given in the table, shows that the polyesters of the first acid generally have the lower softening points. The greatest difference in softening point is shown by polyesters of the first three α,ω-alkanediols. Smaller differences in softening points are shown by polyesters formed by these acids with the long-chain α,ω-alkanediols such as 1,10-decanediol and 1,20-eicosanediol, possibly because all these polyesters are in the crystalline state. Most of the α,ω-alkanediol polyesters of 4,4'-methylenedibenzoic acid are opaque solids, whereas most of the corresponding polyesters of the 3,3' acid are transparent. We observed a similar picture in our earlier comparison of the polyesters of the isomeric benzene- and biphenyl-dicarboxylic acids [1, 2].

TABLE

Polyesters of 4,4'-Methylenedi-, 3,3'-Methylenedi-, and 4,4'-Carbonyldi-benzoic Acids

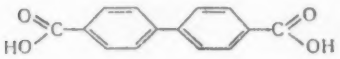
Glycol	4,4'-Methylenedibenzoic acid		3,3'-Methylenedibenzoic acid	4,4'-Carbonyledibenzoic acid	
	Temperature (°C) of				
	thread formation	melting in capillary	thread formation	thread formation	melting in capillary
Ethylene glycol*	136—137 219—221	— 219—221	100—105	318—320	—
1,3-Propanediol	201—207	214—216	73—77	176—180	181—184
1,4-Butanediol	115—120	130—135	43—44	168—175	—
1,5-Pentanediol	37—38	—	51—54	66—68	94—102
1,6-Hexanediol	80—82	90—92	52—56	129—131	130—131
1,10-Decanediol	92—94	95—97	52—54	98—100	101—104
1,20-Eicosanediol	97—103	100—103	65—70	100—108	119—122
1,2-Propanediol	83—84	89—92	65—69	110—111	130—140
1,3-Butanediol	54—56	60—65	38—41	80—85	108—114
Diethylene glycol	80—85	—	58—63	—	—
Triethylene glycol	60—62	—	46—50	—	—

* In the case of the ethylene glycol polyester, amorphous and crystalline samples were obtained. The temperature for thread formation was determined on both samples – the first figure is for the amorphous form and the second for the crystalline.

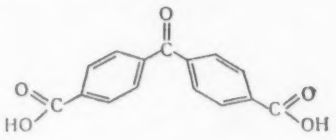
The lower softening temperatures and greater tendency to form amorphous structures found in polyesters of 3,3'-methylenedibenzoic acid can be explained, as in the case of the polyesters of isophthalic and 3,3'-biphenyldicarboxylic acids [1, 2], by the looser packing of the polymer chains due to the less symmetrical structure of the dicarboxylic acids, as compared with the 4,4' isomer. For most of the polyesters given in the Table, replacement of methylene in 4,4'-methylenedi-benzoic acid by carbonyl results in rise in the softening temperature. The greatest difference is found for the ethylene glycol polyesters: the softening point of the polyester of 4,4'-carbonyldibenzoic acid is 100° higher than that of the polyester of 4,4'-methylenedibenzoic acid. The higher softening points of the polyesters of the keto acid can be explained by increased interaction between the chains owing to the presence of the more polar carbonyl group. The introduction of a methylene group or of the more polar carbonyl group between the aromatic nuclei of a biphenyldicarboxylic acid results in lowering of the softening point of the polymer and some increase in its solubility. In the case of the polyesters of methylenedibenzoic acids this behavior is probably to be associated with reduction in the stiffness of the polymer chain, which is enhanced in biphenyldicarboxylic acid by the direct union of the two aromatic nuclei.

The fact that the presence of a keto group between the aromatic nuclei of the dicarboxylic acid does not raise the softening point of the polyester, but, on the contrary, lowers it, suggests that the high softening points of polyethylene terephthalate and polyethylene 4,4'-biphenyldicarboxylate are probably associated with conjugation between the carbonyls of the carboxy groups with the double bonds of the aromatic nuclei with increase in the polarity of the carbonyl groups [3]. In the polyester of 4,4'-carbonyldibenzoic acid this conjugation is broken owing to the presence of the keto group between the aromatic nuclei, which results in lowering of the polarity of the carboxyl carbonyl groups and so in reduced interaction between chains. It is possible also that the low softening points of polyesters of the keto acid as compared with those of the polyesters of 4,4'-biphenyldicarboxylic acid are partly associated with the different shape of the molecule of the keto acid due to the presence of a carbon atom between the aromatic nuclei, as indicated below:

a) structure of 4,4'biphenyldicarboxylic acid



b) structure of keto acid



Comparison of the polyesters of 3,3'-methylenedibenzoic acid with the corresponding polyesters of 3,3'-biphenyldicarboxylic acid shows that, in this case, the introduction of the methylene group between the aromatic nuclei is accompanied by lowering of the softening point of the polyesters (though only slightly in some cases) and some increase in their solubility in benzene and alcohol. This can be explained by reduction in the stiffness of the polymer chain due to the separation of the aromatic nuclei of the acid residues by a methylene group; on the basis of their structural formulas, the densities of packing of the polymer chains in the polyesters of these acids should not be greatly different.

The properties of the polyesters of the methylene- and carbonyl-dibenzoic acids are dependent also on the structure of the glycol. The softening points of the polyesters vary with the number of methylene groups in the glycol. In the series of polyesters of 4,4' acids with α,ω-alkanediols (Table), the polyesters of 5,5'-pentanediol, which are amorphous, have the lowest softening points. Among the polyesters of 3,3-methylenedi-benzoic acid with α,ω-alkanediols the 1,4-butanediol polyester has the lowest softening point. Introduction of a methyl side group into the glycol results in considerable lowering in the melting point of the polyester and, in the case of polyesters of 4,4' acids, in loss in the power to crystallize.

SUMMARY

1. Polyesters of 3,3'-methylenedi-, 4,4'-methylenedi-, and 4,4'-carbonyldibenzoic acids formed with eleven aliphatic glycols of varied structure were synthesized and investigated.

2. On the basis of the results, conclusions are drawn concerning the effect of the structures of the original components on the properties of the polyesters.

LITERATURE CITED

[1] V. V. Korshak, S. V. Vinogradova, and V. M. Belyakov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1957,* 730.

[2] V. V. Korshak, S. V. Vinogradova, and V. M. Belyakov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1957,* 737.

[3] O. Edgar, and R. Hill. J. Pol. Sci. 8, 1 (1952).

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HETEROCHAIN POLYESTERS

COMMUNICATION 7. POLYESTERS OF p-BENZENEDIACETIC AND cis- AND trans-1,4-CYCLOHEXANEDICARBOXYLIC ACIDS

V. V. Korshak, S. V. Vinogradova, and V. M. Belyakov

In a previous communication [1], in explanation of the difference in the softening points of polyesters of 4,4'-carbonyldibenzoic and 4,4'-biphenyldicarboxylic acids, it was suggested that the softening points of polyesters of 4,4'-biphenyldicarboxylic and terephthalic acids are affected by the presence of conjugation between their carbonyl groups and the double bonds of the benzene nuclei, and it was indicated that confirmation of this suggestion may be obtained by investigating, on the one hand, polyesters of a dinuclear dicarboxylic acid having a group that does not break the conjugation introduced between the nuclei and, on the other, polyesters of acids of the type of p-benzenediacetic and 1,4-cyclohexanedicarboxylic acids, in which the conjugation of the carbonyl groups with the double bonds of the nucleus is destroyed. We described compounds of the first type, namely polyesters of 4,4'-azodibenzoic acid, in a previous communication. In the present paper we give results on polyesters of p-benzenediacetic and cis- and trans-1,4-cyclohexanedicarboxylic acids formed with aliphatic glycols of varied structure. The polyesters of the cyclohexanedicarboxylic acids were of interest from the point of view also of the study of the effect of cis-trans isomerism in the original acid on the properties of the polyesters.

TABLE

Polyesters of p-Benzenediacetic and cis- and trans-1,4-Cyclohexanedicarboxylic Acids

Glycol	p-Benzenediacetic acid		trans-1,4-Cyclohexanedicarboxylic acid		cis-1,4-Cyclohexanedicarboxylic acid	
	temp. of thread formation	m. p. in capillary (°C)	temp. of thread formation	m. p. in capillary	temp. of thread formation	m. p. in capillary (°C)
Ethylene glycol	90—92	92—94	64—67	—	—6— —4	—
1,3-Propanediol	50—55	54—58	107—110	—	—	—
1,4-Butanediol	65—70	78—80	130—135	133—137	87—94	92—97
1,5-Pentanediol	33—34	33—36	40—45	—	—9— —7	—
1,6-Hexanediol	55—58	65—67	102—104	105—107	64—69	67—71
1,10-Decanediol	67—69	66—69	94—97	95—97	78—81	78—80
1,20-Eicosanediol	80—86	86—87	100—105	102—105	94—96	94—96
1,2-Propanediol	39—41	39—41	47—50	66—68	—	—
1,3-Butanediol	0—2	—	18—23	—	—	—
Diethylene glycol	4—8	—	25—30	—	—15÷—13	—
Triethylene glycol	—4÷0	—	—9÷—6	—	—26÷—24	—

The use of aliphatic glycols of varied structure in the synthesis of the polyesters of these acids made it possible to follow the change in the properties of the polyesters in their dependence on the structure of the glycol. There is some information in the literature on the polyesters of 1,4-cyclohexanedicarboxylic and p-benzenediacetic acids [2-5], but its disconnected sporadic character often precludes the possibility of comparisons.

The table gives data on the polyesters of p-benzenediacetic and cis- and trans-1,4-cyclohexanedicarboxylic acids. Comparison of these polyesters with the corresponding polyesters of terephthalic acid [6] shows that all the terephthalic polyesters that we prepared have higher softening points. Thus, the softening points of the 1,4-butanediol polyesters of terephthalic, p-benzenediacetic, and trans-1,4-cyclohexanedicarboxylic acids are 222°, 78° and 133°, respectively . This difference between the terephthalic polyesters and the trans-1,4-cyclohexanedicarboxylic and p-benzenediacetic polyesters appears to prove the presence in terephthalic acid of a conjugated system of double bonds formed by the aromatic nucleus with the carbonyl groups with resulting increased polarity of the carbonyl groups, which, in its turn, results in increased interaction between chains. The breaking of this conjugation by hydrogenation of the aromatic nucleus or displacement of the aromatic nucleus away from the carboxyls results in a sharp change in the properties of the polyesters: lowering of softening points and temperatures of transition into the viscous liquid state, and increase in solubility. The higher softening points of trans-1,4-cyclohexanedicarboxylic polyesters, as compared with the corresponding adipic polyesters [7], shows that replacement of the aliphatic acid by the alicyclic acid increases the softening point of the polymer, evidently owing to the higher stiffness of a polymer chain containing a hydrogenated nucleus in which the carboxy groups are in the trans-para positions.

Comparison between cis-and trans-1,4-cyclohexanedicarboxylic polyesters shows that the cis polyesters have lower temperatures for thread and glass formation. Thus, for ethylene glycol polyesters the difference in glass points is 32° – the trans polyester is a clear somewhat elastic almost solid product, whereas the cis polyester is a viscous liquid. The difference in the cis-and trans polyesters is doubtless associated with the difference in the relative dispositionof the carboxy groups of the acid with respect to the plane of the cyclohexane nucleus. The less symmetrical cis acid forms a polymer in which the polymer chains are more loosely packed than in that formed from the more symmetrical trans acid. This results in lowering of softening point, increase in solubility, and greater readiness to form an amorphous structure.

The properties of the polymers are affected also by change in the structure of the glycol. Thus, in the series of p-benzenediacetic polyesters we have a picture similar to that observed for other aromatic dicarboxylic polyesters having the carboxyls in para positions [6, 8]. Polyesters of glycols having an even number of methylenes melt higher than their "odd" neighbors. The introduction of a methyl side group or ether linkage into the glycol molecule is accompanied by lowering of the softening point of the polymer and sometimes also the elimination of crystallinity.

The p-benzenediacetic and trans-1,4-cyclohexanedicarboxylic polyesters were obtained by polycondensation of the dimethyl esters with the glycols in the melt. In the synthesis of the cis-1,4-cyclohexanedicarboxylic polyesters, the polycondensation was carried out in toluene solution and the polyester was isolated by precipitation with petroleum ether. cis- and trans-1,4-Cyclohexanedicarboxylic acids were synthesized by hydrogenation of dimethyl terephthalate under pressure in presence of Raney nickel. The isomers were separated by Batzer's method [4].

SUMMARY

1. Polyesters formed by p-benzenediacetic and cis- and trans-1,4-cyclohexanedicarboxylic acids with glycols of various structures are described.

2. The effects on the properties of the polyesters of the structure of the glycol, cis-trans-isomerism in the acid , the displacement of the carboxy groups away from the aromatic nucleus, and the replacement in the acid of an aromatic nucleus by an alicyclic nucleus are discussed.

LITERATURE CITED

[1] V. V. Korshak, S. V. Vinogradova, and V. M. Belyakov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1957, * 998.

[2] O. B. Edgar, and R. Hill, J. Pol. Sci. 8, 1 (1952).

[3] H. J. Kolb, and E. F. Izard, J. Appl. Phys. 20, 564 (1949).

[4] H. Batzer, and G. Fritz, Makromol. Chem. 14, 179 (1954).

* In Russian.

[5] H. Batzer, and G. Fritz, Makromol. Chem. 11, 85 (1953).

[6] V. V. Korshak, S. V. Vinogradova, and V. M. Belyakov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1957, * 730.

[7] V. V. Korshak, S. V. Vinogradova, and E. S. Vlasova, Proc. Acad. Sci. USSR 94, 61 (1954).

[8] V. V. Korshak, S. V. Vinogradova, and V. M. Belyakov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1957, * 737.

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HETEROCHAIN POLYAMIDES

COMMUNICATION 2. KINETIC PECULIARITIES OF THE POLYCONDENSATION OF DIAMINES WITH DICARBOXYLIC ACIDS

V. M. Kharitonov, T. M. Frunze, and V. V. Korshak

The kinetics of the polycondensation of diamines with dicarboxylic acids have been studied by various investigators. Thus, Korshak and Rafikov [1] showed for the case of the polycondensation of adipic acid with 1,6-hexanediamine that removal of the water formed in the reaction mixture makes it possible to obtain a product of considerably higher molecular weight. The kinetics of the polycondensation of 1,6-hexanediamine with sebacic acid were studied by Chelnokova, Rafikov, and Korshak [2], who found that above 160° reaction proceeds by a bimolecular mechanism, the activation energy being 24,000 cal/mole.

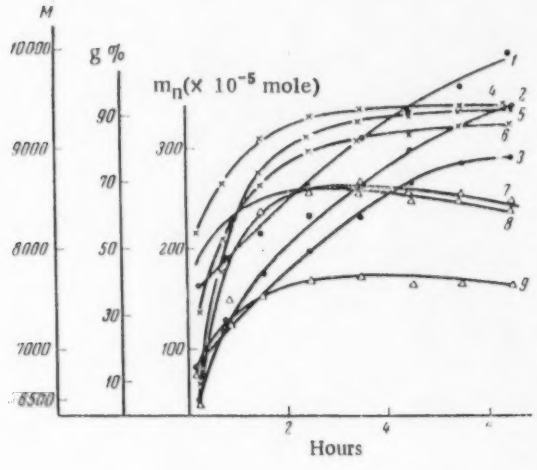

Fig. 1. Relation of the molecular weight (M), yield (g), and number of moles (m_n) of polyhexamethyleneadipamide to the duration of reaction at various temperatures and concentrations of original monomers:
1, 4, 8 – M, g, and m_n, respectively, at 205° and 15%
2, 5, 7 – M, g, and m_n, " , at 195° and 15%
3, 6, 9 – M, g, and m_n, " , at 205° and 10%.

The object of the investigation was the study of the effect of the structure of the dicarboxylic acid on the kinetic laws of polyamide formation with diamines. For the polycondensation we used carefully purified 1,6-hexanediamine adipate (HA salt), m.p. 192-194°, and 1,6-hexanediamine azelaate (HAz salt), m.p. 150-152°. Reaction was carried out in solution in cresol (mixture of isomers) with concentrations of the original components of 10% and 15% and temperatures of 195° and 205° in an atmosphere of purified nitrogen. Polymer and unchanged monomer were isolated from test samples by precipitation, for which purpose a 30-fold excess of boiling benzene was added [3, 4]. The precipitate was filtered off and carefully washed with benzene. Monomer was removed from the precipitate by aqueous extraction at room temperature. The results are given in the Table and in Figures 1 and 2.

For both HA salt and HAz salt the yield of polyamide rose continuously as reaction progressed (Fig. 2). The rise in yield was accompanied by continuous rise in mean molecular weight. In the early stage of the process there was a rapid increase in the number of moles of polyamide formed, which indicates a predominance of the mechanism of chain growth at the expense of monomer. As the original monomers became exhausted in the reaction medium, a point was attained at which condensation of the polymer molecules already formed began to predominate. This point is characterized by diminution in the number of moles of polyamide formed and simultaneous rapid rise in its molecular weight (Figures 1 and 2). The position of the maximum on the curve for the variation in

the number of moles of polyamide in the polycondensation of the given monomers (HA and HAz salts) does not depend on their structures, but on the progress of reaction and the molecular weight. The position of the maximum depends also on the concentration of the original monomers.

Kinetics of Polyamide Formation

Duration of reaction (hours)	Reaction temperature (°C)	Concentration of original reaction components (%)	Amount of polyamide formed (× 10^{-5} mole)		Rate of change of the number of moles of polyamide (× 10^{-5} mole/hour)		Degree of polymerization of polyamide from HA salt K_I	Degree of polymerization of polyamide from HAz salt K_{II}	$\frac{K_I}{K_{II}}$
			from HA salt	from HAz salt	from HA salt	from HAz salt			
0.25	195	15	44.6	—	—	—	28.9	—	—
0.75			150.9	206.7	—	—	31.4	—	—
1.5			239.6	226.9	—	—	34.2	30.4	1.13
2.5			256.7	266.4	—	—	36.9	30.7	1.20
3.5			264.3	261.8	2.3	3.6	38.1	32.3	1.18
4.5			256.2	255.5	—	—	39.8	33.8	1.18
5.5			251.2	248.8	—	—	40.8	35.0	1.16
6.5			247.6	245.9	—	—	41.7	35.6	1.17
0.25	205	15	180.0	201.9			33.8	28.7	—
0.75			221.6	234.0			34.9	30.6	—
1.5			256.3	249.8			36.0	31.4	1.15
2.5			261.0	256.9			38.3	33.1	1.16
3.5			253.8	252.6	5.5	6.0	40.2	34.7	1.16
4.5			248.7	246.9			41.3	36.0	1.15
5.5			254.5	241.8			42.5	37.2	1.14
6.5			238.9	232.8			44.0	38.8	1.14

The rate of growth of macromolecules by intercondensation, which is observed in the final stage of the process, is directly related to the conditions under which the process is carried out. Rise in the initial concentration of monomers and the reaction temperature increases the possibility of the condensation of macromolecules among themselves (Figs. 1 and 2). Thus, when the maximum number of moles of polyamide has been attained (in the polycondensation of HA and HAz salts at 195° and 205° and an initial concentration of 15%), the rate of condensation of macromolecules will be greater, the higher the temperature of the process (Figs. 1 and 2). The rate of rise in molecular weight at this stage of the process does not depend on the nature of the polyamide. It will be seen from the Table that the rate at which the number of polymer molecules diminishes (after 2.5 hours of reaction) is approximately the same for both of the polyamides investigated.

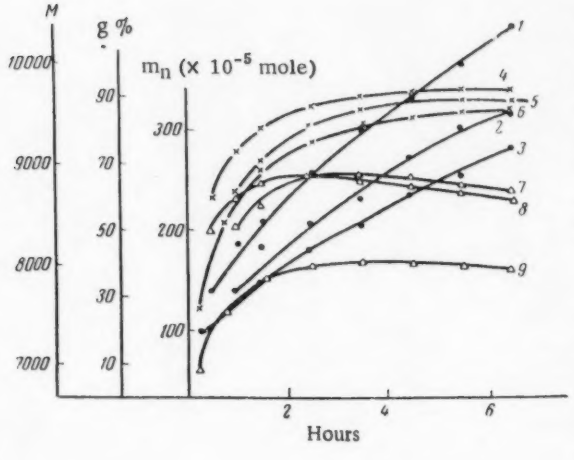

Fig. 2. Relation of the molecular weight (M), yield (g), and number of moles (m_n) of polyhexamethyleneazelaamide to the duration of reaction at various temperatures and concentration of original monomers:
1, 4, 8 – M, g, and m_n, respectively, at 205° and 15%
2, 5, 7 – M, g, and m_n, " , at 195° and 15%
3, 6, 9 – M, g, and m_n, " , at 205° and 10%.

In the polycondensation, growth of the polyamide chain of the macromolecule proceeds in two ways: 1) direct addition of monomer residues to growing macromolecules; 2) condensation of the macromolecules among themselves. The structures of the original components have no substantial effect on the rate of polyamide chain growth. In both cases the reaction is subject to second-order laws and is associated with an activation energy of 16,800 cal/mole in the case of 1,6-hexanediamine adipate and of 20,900 cal/mole in the case of 1,6-hexanediamine azelaate.

SUMMARY

1. Investigation of the polycondensation of 1,6-hexanediamine adipate and of 1,6-hexanediamine azelaate showed that the changes in rate of polyamide formation and in rise of molecular weight are identical in character in both cases at a given temperature and concentration of reactants.

2. It was found that the polycondensation of 1,6-hexanediamine salts of dicarboxylic acids proceeds as a second-order reaction. Activation energies were determined for these processes.

LITERATURE CITED

[1] V. V. Korshak and S. R. Rafikov, J. Gen. Chem. 14, 983 (1944).

[2] G. N. Chelnokova, S. R. Rafikov, and V. V. Korshak, Proc. Acad. Sci. USSR 64, 353 (1949).

[3] T. M. Frunze, Thesis, Inst. Org. Chem. Acad. Sci. USSR, 1952.

[4] E. A. Meos, Thesis, Leningrad Textile Inst., 1953.

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REACTION OF 2-METHYL-2-PHENYLPROPYLMAGNESIUM CHLORIDE WITH ALLYL AND 2-METHYLALLYL CHLORIDES

A. D. Petrov, O. M. Nefedov, and Yu. N. Ogibin

The synthesis of tert-alkylbenzenes has been effected mainly by the Friedel-Crafts reaction [1], but the use of aluminum chloride as catalyst does not guarantee that the hydrocarbons obtained will be pure. It was in fact recently found by Huston [2] that, in the alkylation of benzene with 3,4-dimethyl-3-hexanol in presence of aluminum chloride, a mixture of six (!) different isomeric tert-octylbenzenes was formed. In the present investigation, therefore, we attempted to synthesize branched heptyl- and octyl-benzenes by the Grignard reaction from 2-methyl-2-phenylpropyl chloride. It is known that n-octylbenzene and n-heptylcyclohexane have freezing points of − 45° [3] and −41° [4] respectively. It was of interest to determine the freezing points of their isomers with branched alkyl chains.

The Grignard reagent from 2-methyl-2-phenylpropyl chloride − a structural analog of neopentyl chloride − was prepared recently, and it was established that it is able to condense with carbonyl compounds (heptanal) [5]. The behavior of this Grignard reagent in the Grignard-Wurtz reaction has not yet been studied. We showed that 2-methyl-2-phenylpropylmagnesium chloride is unable to condense with saturated alkyl halides (isobutyl chloride and bromide), but condenses in good yield (50-70%) with 2-alkenyl halides (allyl and 2-methylallyl chlorides). The resulting alkenylbenzenes were hydrogenated over Raney nickel and so converted into the corresponding tert-alkylbenzenes (50 atm, about 20°, 10-12 hours) and alkylcyclohexanes (initial hydrogen pressure 120-140 atm, 180-200°, 10-12 hours). In all experiments there also occurred partial condensation of the original 2-methyl-2-phenylpropyl chloride in presence of magnesium into 2,5-dimethyl-2,5-diphenylhexane (yield 5-7%), which was hydrogenated to the corresponding dicyclohexylalkane. The kinematic viscosities of the hydrocarbons obtained were determined, and it was found that alkylcyclohexanes have higher (by about 50%) viscosities than the corresponding hydrocarbons of the benzene series. The properties of the hydrocarbons synthesized are given in the Table.

EXPERIMENTAL

2-Methyl-2-phenylpropyl chloride was prepared by the alkylation of benzene with 2-methylallyl chloride (b.p. 71-72°; n_D^{20} 1.4269; d_4^{20} 0.9228) in presence of concentrated sulfuric acid, yield 75-80%; b.p. 81-82° (6 mm), 110° (20 mm); n_D^{20} 1.5238; d_4^{20} 1.0420. The literature [6] gives b.p. 97-98° (10 mm); n_D^{20} 1.5250.

Reaction of 2-methyl-2-phenylpropyl chloride with isobutyl halides. A solution of 139 g (1.5 moles) of isobutyl chloride in 150 ml of ether was added over a period of four hours to 2-methyl-2-phenylpropylmagnesium chloride prepared in 88% yield from 84.3 g (0.5 mole) of 2-methyl-2-phenylpropyl chloride and 15.8 g (0.65 g-atom) of magnesium in 200 ml of ether. The reaction mixture was stirred for 20 hours at the boiling point of ether, and was then decomposed with 10% hydrochloric acid and treated in the usual way. From the reaction products, after three hours at the boil over sodium, 53 g (80%) of tert-butylbenzene, b.p. 163-166° (749 mm) and n_4^{20} 1.4928, was isolated. The literature [7] gives b.p. 169.5° (760 mm; n_D^{20} 1.4926; d_4^{20} 0.8666[7].

Treatment of the Grignard reagent from 67.2 g (0.4 mole) of 2-methyl-2-phenylpropyl chloride and 12.2 g (0.5 g-atom) of magnesium in 300 ml of ether with a solution of 110 g (0.8 mole) of isobutyl bromide in 150 ml of ether (three hours) and subsequent stirring of the mixture (35°, nine hours) again gave only 2,5-dimethyl-2,5-diphenylhexane and tert-butylbenzene; yield 45 g (84%); b.p. 68-71° (30 mm); n_D^{20} 1.4919; d_4^{20} 0.8658.

TABLE

Properties of Hydrocarbons Synthesized

Hydrocargon	Formula	B. p. in °C	F. p. (°C)	n_D^{20}	d_4^{20}	*MR* found	*MR* calc.	Kinematic viscosity ν (centistokes) 20°	50°	100°	Elementary analysis found % C	H	calculated % C	H
5-Methyl-5-phenyl-1-hexene	$C_{13}H_{18}$	71 (3)	—	1.5043	0.8848	58.35	58,25	—	—	—	89.56 89.60	10.55 10.48	89.59	10.41
2,5-Dimethyl-5-phenyl-hexene	$C_{14}H_{20}$	99 (7)	—	1.5074	0.8874	63.19	62.84	—	—	—	89.36 89.26	10.75 10.78	89.29	10.71
2-Methyl-2-phenyl-hexane	$C_{13}H_{20}$	70 (3)	—89 (glass)	1.4906	0.8675	58.82	58.67	2.38	1.38	0.77	88.59 88.75	11.45 11.38	88.56	11.44
2,5-Dimethyl-5-phenyl-hexane	$C_{14}H_{22}$	78 (3)	—74 (glass)	1.4885	0.8653	63.42	63.35	3.32	1.74	0.96	88.15 88.24	11.58 11.76	88.35	11.65
2-Cyclohexyl-2-methyl-hexane	$C_{13}H_{26}$	90,5 (6)	—87 (glass)	1.4582	0.8330	59.75	59.79	3.56	1.90	0.99	85.44 85.60	14.59 14.50	85.63	14.37
2-Cyclohexyl-2,5-dimethylhexane	$C_{14}H_{28}$	85,5 (3,5)	—83 (glass)	1.4634	0.8446	64.08	64.47	5.10	2.52	1.23	85.62 85.80	14.30 14.33	85.63	14.37
2,5-Dimethyl-2,5-diphenylhexane	$C_{20}H_{26}$	—	M. p. +62° (from alcohol)	—	—	—	—	—	5.03 (75°)	2.96	90.25 90.25	9.89 9.91	90.16	9.84
2,5-Dicyclohexyl-2,5-dimethylhexane	$C_{20}H_{38}$	—	M. p. +83° (from alcohol)	—	—	—	—	—	—	5.00	86.41 86.35	13.85 13.80	86.25	13.75

Reaction of 2-Methyl-2-phenylpropyl chloride with allyl and 2-methylallyl chlorides. A solution of 67.2 g (0.4 mole) of 2-methyl-2-penhylpropyl chloride in 150 ml of ether was added over a period of 2.5 hours to 12.2 g (0.5 g-atom) of magnesium in 150 ml of ether. Stirring was continued for one hour, and a solution of 76.5 g (1.0 mole) of allyl chloride (b.p. 44-45°; n_D^{20} 1.4153) in 150 ml of ether was added over a period of 90 minutes, after which the reaction mixture was stirred further for eight hours at the boiling point of ether. After the usual treatment ether was distilled off. Fractionation of the residue, first through a 15-plate column under atmospheric pressure (up to 200°) and then under reduced pressure, gave 7 g of 1,5-hexadiene, 18 g of tert-butylbenzene, and also 50 g of a fraction of b.p. 102-106° (10 mm), n_D^{20} 1.5050; d_4^{20} 0.8930. Boiling of this fraction over sodium for four hours gave pure 5-methyl-5-phenyl-1-hexene in a yield of 48.5 g (70%).

Similarly, by addition of a solution of 90.5 g (1.0 mole) of 2-methylallyl chloride in 150 ml of ether over a period of one hour to the Grignard reagent obtained from 87 g (0.52 mole) of 2-methyl-2-phenylpropyl chloride and 14.6 g (0.6 g-atom) of magnesium in 300 ml of ether with subsequent stirring 12 hours at 35°, we synthesized 2,5-dimethyl-5-phenyl-1-hexene in a yield of 50.5 g (51%); it was purified by boiling it over sodium for four hours and subsequent fractionation. From the reaction products we isolated also 2,5-dimethyl-1,5-hexadiene (12 g), tert-butylbenzene (20 g), and 2,5-dimethyl-2,5-diphenylhexane (3.2 g).

SUMMARY

1. It was shown that 2-methyl-2-phenylpropylmagnesium chloride does not react with isobutyl halides, but it condenses with allyl and 2-methylallyl chlorides with formation of the corresponding hydrocarbons in high yield (70% and 51%).

2. The freezing points of the branched alkylbenzenes and alkylcyclohexanes synthesized range from -70° to -90° and are lower by 30-45° than the freezing points of the isomeric hydrocarbons having normal paraffin chains.

LITERATURE CITED

[1] E. Schreiner, J. prakt. Chem. 82, 292 (1910); O. Halse, J. prakt. Chem. 89, 451 (1914); R. Huston et al,. J. Org. Chem. 3, 251, 351 (1938); 6, 252 (1941); 11, 657 (1946); 13, 63 (1948); 18, 620 (1953).

[2] R. Huston, et al., J. Am. Chem. Soc. 70, 1090 (1948).

[3] R. Paquette, E. Lingafelter, and H. Tartar, J. Am. Chem. Soc. 65, 686 (1943).

[4] A. Schmidt, and A. Grosser, Ber. 73, 930 (1940).

[5] V. Weinmayr, US Patent 2467170; C. A. 43, 6232 (1949).

[6] W. Smith jun. and D. Sellas, Organic Syntheses, Collection 4 (Russian Translation), Moscow, Foreign Lit. Press. 1953, p. 526.

[7] S. Birch, R. Dean, F. Fidler, and R. Lowry, J. Am. Chem. Soc. 71, 1361 (1949).

D. I. Mendeleev Institute of Chemical Technology
Moscow and N. D. Zelinsky Institute of Organic
Chemistry of the Academy of Sciences of the USSR

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LETTERS TO THE EDITOR

SYNTHESIS OF RACEMIC SARKOMYCIN

Dear Editor

We recently synthesized an isomer, 3-methylene-4-oxocyclopentanecarboxylic acid, of the antitumor antibiotic sarkomycin, 2-methylene-3-oxocyclopentanecarboxylic acid. We have now synthesized the racemate of sarkomycin itself (IV, X = O), which, in view of its instability, was prepared in the form of its semicarbazone.

$$CH_3-CHC(COOEt)_2(CH_2)_2C=X\ (I) \rightarrow CH_2=CC(COOEt)_2(CH_2)_2C=X\ (II) \rightarrow$$
$$\rightarrow YCH_2-CHC(Z)(Z')(CH_2)_2C=X\ (III) \rightarrow CH_2=CCH(COOH)(CH_2)_2C=X\ (IV).$$

The starting material (I) (X = $NNHCONH_2$) (b. p. 195-196°; found %: C 52.52; H 6.70; N 14.14), was converted, by the action of Br_2 and then Et_3N (15-20°) into (II) (X = $NNHCONH_2$) (decomp. 207-209°; found %: C 52.45; H 6.38; N 14.02), which with Me_2NH (25°, 100 hours) gave the amine (III) (X = $NNHCONH_2$; Y = = Me_2N; Z = Z' = COOEt) (m.p. 160-161°; found %: C 52.70; H 7.74; N 16.48), which was hydrolyzed by $Ba(OH)_2$ (25°, 36 hours) to the acid (III) (X = $NNHCONH_2$; Y = Me_2N; Z = Z' = COOH) (decomp. above 200°; found for monohydrate %: C 43.42; H 6.63; N 18.40). The last compound was converted (quinoline, 120°, 1 hour) into the acid (III) (X = $NNHCONH_2$; Y = Me_2N; Z = H; Z' = COOH) (decomp. above 200°; found %: C 49.39; H 7.94; N 22.83), and further by CH_2N_2 into the ester (III) (X = $NNHCONH_2$; Y = Me_2N; Z = H; Z' = COOMe) (decomp. above 200°; found %: C 51.35; H 7.75) which with MeI (50°, 20 minutes) gave the methiodide (III) (X = $NNHCONH_2$; Y = $Me_3\overset{+}{N}I^-$; Z = H; Z' = COOMe) (decomp. 187-188°). This gave a picrate (m.p. 160-161°; found %: C 42.81; H 4.56) and was hydrolyzed (10% Na_2CO_3, 15 minutes, 60°; and then HI) to the acid (III) (X = $NNHCONH_2$; Y = $Me_3\overset{+}{N}I^-$; Z = H; Z' = COOH) (decomp. 176°-178°; found %: C 34.20; H 5.72). When this acid was heated with 1 NaOH (2.35 moles, 4 minutes, 95°), subsequent acidification gave a precipitate of the semicarbazone of racemic sarkomycin (IV) (X = $NNHCONH_2$) in admixture with the semicarbazone of the isomeric 2-methyl-3-oxo-1-cyclopentene-1-carboxylic acid. This substance decomposes slowly above 200°; it took up one molecular proportion of Br_2 in acetic acid; AcOH; found %: C 48.87; H 6.02; the position of the double bond was proved by ozondysis.

Institute of Biological and Medical Sciences
of the Academy of Medical Sciences of the USSR

M. M. Shemyakin, G. A. Ravdel,
E. S. Chaman, Yu. B. Shvetsov, and
E. I. Vinogradova

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CURRENT EVENTS

GENERAL MEETING OF THE DIVISION OF CHEMICAL SCIENCES OF THE ACADEMY OF SCIENCES OF THE U.S.S.R, JANUARY 22, 1957

At a general meeting of the Division of Chemical Sciences of the Academy of Sciences of the USSR held on January 22, 1957, under the chairmanship of Academician A. P. Vinogradov elections were held for the posts of academician-secretary of the Division and members of the Bureau. Academician N. N. Semenov was elected as academician secretary. Academicians B. A. Arbuzov, A. P. Vinogradov, S. I. Volfkovich, M. M. Dubinin, V. N. Kondratyev, A. N. Terenin, and A. N. Frumkin and Corresponding Members of the Academy N. M. Zhavoronkov and M. M. Shemyakin were elected as members of the Bureau.

The members expressed their thanks to Academician M. M. Dubinin for his many years of valuable work as academician-secretary of the Division.

At a general meeting of the Division held on April 26, 1957, the following were elected as assistant academician-secretaries: Academician A. P. Vinogradov (First Assistant) and Corresponding Members of the Academy N. M. Zhavoronkov and M. M. Shemyakin.

* * *

An ordinary general meeting of the Division was held on April 25-26, 1957, under the chairmanship of Academician N. N. Semenov.

Corresponding Member of the Academy K. A. Kocheshkov (co-worker V. P. Glushkova) read a paper on "Metallation (Thallation) of Organic Compounds." He pointed out that one of the principal methods for the synthesis of certain organometallic compounds consists in direct replacement of hydrogen by M or MX (M is a metal and X an acid residue). This is the way in which, for example, "mercuration," "auration," and "lithation" are carried out. The thallation reaction has remained uninvestigated. The reaction, described briefly by Gilman (US), of direct introduction of thallium (by the action of thallium trichloride) into dibenzofuran has received no further development in the fifteen years that have passed since its discovery, owing to the low yields, severe conditions, and probable occurrence of secondary reactions.

The author reported that, as a result of his investigations, the thallation of organic compounds of various classes by means of thallium salts of organic acids may now find extensive application. With respect to some of his main results, in particular with respect to the type of compounds obtained, the orientation of the reaction, and the readiness with which it occurs, thallation under the given conditions did not accord with the results of the American workers. In the thallation of dibenzofuran the formation of compounds of the type $ArTlX_2$ – and not Ar_2TlX as found by Gilman – was proved by their conversion into derivatives of chloroacetic acid. Orientation into the p-position with respect to the oxygen atom of dibenzofuran was confirmed by conversion into the corresponding iodide and further into the monocarboxylic acid. Thallation occurred at 100° in 50% yield, instead of 9% (at 165°), as found by the American workers. Benzene was thallated almost quantitatively at 100° (18 hours) with the aid of thallium triisobutyrate. In spite of the use of excess of benzene, compounds of the type $ArTlX_2$ were always obtained. In special experiments under more severe conditions no polythallation could be detected (contrast polymercuration).

Thallation of toluene (1 hour at 100°; yield 50%) proceeds mainly in the p-position. Thallation of naphthalene (1 hour at 110°; yield 50%) occurs in the 1-position. Thallium can be introduced into phenol and polyphenol ethers. Thiophene can be thallated extremely readily (2-position; yield 88% in 5 minutes). On the other hand, furan is oxidized when treated with tervalent thallium salts. The author stated that, as he had

tervalent thallium salts of various organic acids at his disposal, he had investigated their behavior in various reactions, in particular, reactions with unsaturated compounds (cyclohexene).

Academician A. N. Nesmeyanov and Corresponding Members of the Academy V. I. Spitsyn, A. E. Kapustinsky, and S. Z. Roginsky participated in the discussion on this paper.

A paper on "Surface Phenomena in Ternary Metallic Systems" was read by Dr. V. K. Semenchenko (co-workers P. P. Pugachevich and V. B. Lazarev). The author stated that work on the surface tension of liquid metal and salt solutions had established a parallelism between this property and the microstructure, microhardness, recrystallization, and polymorphous transitions of the crystalline aggregate formed from the melt. All the results obtained, however, refer to binary systems. As most of the systems of technical importance consist of three or more components it was essential to investigate such systems.

The molecular theory of surface phenomena developed by the author is applicable also to multicomponent system. Investigation of the surface tension of ternary systems – solutions of electrolytes in dielectrics – revealed the phenomenon of concentration and temperature buffer effects, explicable on the molecular theory of surface phenomena.

In order to elucidate the question of the identical character of surface phenomena in ternary metal and dielectric systems, studies were made of surface tension in the systems Cd–Hg–K and Cd–Hg–Ca, Cd being surface-inactive on mercury and K and Ca surface-active. In this case more general conclusions can be reached, because a multicomponent system can be regarded as a generalized ternary system. The surface tension of these systems was investigated in P. P. Pugachevich's combined apparatus. In all, 266 amalgams were investigated at 22°; the Cd content ranged from 0 to 7.13 atoms %, the K content from 0 to 0.6 atom %, and the Ca content from 0 to 0.36 atom %. The investigation revealed the presence of a concentration buffer effect in both systems, the buffered surface tension being almost the same in both systems and the buffering concentration being considerably less for Ca than for K. It was found that adsorption of surface-active metal increases with increase in the concentration of surface-inactive metal and the maximum adsorption has a tendency to be displaced toward the lower concentrations, as follows from the molecular theory of surface phenomena. Comparison of results obtained in the investigation of the surface tension of Cd–K and Cd–Cs amalgams with results on the ternary systems – solutions of electrolytes in dielectric liquids – indicates the generality of the character of processes of adsorption in various classes of solutions.

Academician A. N. Frumkin and Drs. A. V. Kiselev, S. Z. Makarov, and V. I. Mikheeva participated in the discussion on this paper.

A paper on "Some Reactions in Liquid Ammonia in presence of Oxygen under Pressure" was read by Dr. V. G. Tronev (co-workers V. N. Chulkov and A. L. Khrenova). The author stated that in recent years carrying out reactions in presence of gases (oxygen, ammonia, hydrogen, etc.) under high pressure had found industrial application in the "complex" extraction of metals from sulfide concentrates. However, the chemistry of processes in sulfide – ammonia – water – oxygen systems at high pressure had received inadequate study, and such reactions in anhydrous ammonia had not been investigated at all.

The author undertook experiments on the oxidation of sulfur in liquid ammonia in presence of oxygen at high pressure with the object of isolating individual products obtained in absence of water; the results were compared with reactions previously studied in an aqueous-ammoniacal medium. V. G. Troney pointed out that, under ordinary conditions of temperature and pressure, neither sulfur, sulfides, nor ammonia, taken separately, react with oxygen, but when all are present together under pressure oxidation begins at ordinary temperature with evolution of heat and proceeds at a considerable rate, probably owing to the formation of free radicals and the operation of a chain mechanism. The sulfur-nitrogen compound formed in the oxidation of sulfur contains, S, N, and O in the proportions 4:5:8, is readily soluble in water, and contains about 21% of nitrogen in the amine form, with some nitrate impurity. The formation of nitrates in the oxidation of liquid ammonia by oxygen under pressure is observed also in presence of silver powder, which passes into a silver aminonitrate at 50-100°. Similar reactions occur in presence of selenium, tellurium, germanium, etc. The author said that it was desirable to continue the study of the composition, structure, and physicochemical properties of compounds obtained in liquid ammonia in presence of oxygen under pressure with the object of elucidating the chemistry of these reactions and exploring the possibilities of their practical use.

Academician S. I. Volfkovich and N. N. Semenov joined in the discussion of this paper.

In a paper on "Some Questions of the Conformation of Organic Compounds," Academician B. A. Arbuzov stated that recent years were characterized by substantial progress in the study of the steric structure of organic compounds, particularly cyclic compounds. He pointed out that the spatial disposition of individual groups in molecules of the tetrahedral or pyrimidal types was generally examined for simple organic compounds, whereas the disposition in space of carbon chains containing several carbons and attached to a central atom had been studied and discussed to an extremely inadequate extent.

Studies in the Butlerov Institute, Kazan University, of esters of the acids of phosphorus, boron, silicon, etc. by parachor and viscosity methods led to the view that the alkoxy chains are disposed in a definite way in space. Dipole moment determinations on compounds of this type gave values in good agreement with calculated values for completely free rotation of the unsymmetrical groups. However, calculations showed that in most of the compounds studied the completely free rotation of the unsymmetrical groups is scarcely possible on steric grounds. On the basis of a large amount of experimental meterial the author concluded that the agreement of experimental values of the dipole moment with those calculated from formulas for completely free rotation does not prove that the symmetrical and unsymmetrical groups can rotate with complete freedom and that this question needs to be re-examined. The author said that a synchronized vibrational or rotary motion of the alkyl or alkoxy chains on the central atom must be regarded as most probable.

Data on the conformation of pentaerythritol and analogous substances were examined. B. A. Arbuzov stated that the disposition and degree of branching of hydrocarbon chains can have a great effect on the physical and some chemical properties of compounds. This was illustrated by examples of alkoxides and certain amines. From his study of cyclic esters of phosphorous, sulfurous, and other acids by the dipole moment method, the author derived the conformations of five- and six-membered rings in compounds of these types. On the basis of the examination of the parachors of some ring compounds, suggestions were made regarding their conformations. In conclusion, B. A. Arbuzov pointed out that further work on the elucidation of the many important questions on the spatial disposition and the movements of individual groups in organic molecules demanded the combined efforts of organic chemists, physical chemists, physicists, and mathematicians.

Corresponding Members of the Academy Ya. K. Syrkin and B. V. Nekrasov, Prof. G. V. Chelintsev, Dr. A. I. Kitaigorodsky, Corresponding Member of the Academy S. N. Danilov, and Dr. Ya. L. Goldfarb participated in the discussion on this paper.

Dr. V. V. Voevodsky read a paper on the method of electronic paramagnetic resonance for the solution of certain chemical problems.

This method, discovered and developed in 1944 by E. K. Zavoisky in Kazan, makes it possible under certain conditions to investigate the behavior of particles having unpaired electrons. From the frequency of the paramagnetic absorption line and from its form and breadth, certain conclusions can be drawn concerning the properties of the paramagnetic particle. The density of the absorption line can serve as a measure of the concentration of particles of this sort. When the sphere of influence of an unpaired electron contains atoms having nuclear moments that differ from zero, the absorption line assumes a fine structure. From the number of components in the multiple structure and their relative intensities, a direct estimate can be made of the distribution of free electron density among various atoms of the paramagnetic particle. The apparatus used consists in an electromagnet (H = 3000 gauss), a generator of centimeter waves, waveguides, a resonator, and a detecting device. Variations are produced in the high-frequency power required in the reorientation of the spin magnetic moment of a free electron interacting with a constant field H.

The method of electronic paramagnetic resonance was applied by the author in the investigation of the structure of certain paramagnetic particles in the solid and liquid phases, and also in the investigation of the variation in the concentration of free radicals in the course of chemical processes. The following compounds, which were synthesized in Prof. G. A. Razuvaev's laboratory in the Gorky State University, were investigated: $(C_6H_6)_2CrI$, $(C_6H_5-C_6H_5)_2CrI$, and $(C_6H_5-C_6H_5)_2CrOC_6H_5$. They all give intense absorption, corresponding to one unpaired electron. The author drew attention to the case of the dibiphenyl compounds; these gave an absorption line in solution which had a fine structure of nine components, which indicates that the free electron is able to interact with the hydrogens of the addends, since the hydrogens are the only atoms in the molecule that have nuclear moments.

The method of electronic paramagnetic resonance, said V. V. Voevodsky, opens new propects for the precise quantitative measurement of defects arising in solids under the action of ionizing radiations. Thus, the author was the first to investigate the changes occurring in quartz exposed to γ - and x-rays by this method. It was shown that the paramagnetic defects formed in fused quartz in this way result from the capture by non-paramagnetic defects of electrons and electron-holes produced by ionization. One of the advantages of the method is the possibility that it affords the following changes in the concentration of free radicals in the course of rapid chemical processes. Two examples of this have been investigated. The first concerns the kinetics of the adsorption of oxygen and nitric oxide on various charcoals. The adsorption was determined from the reduction in the number of free valences on the surface of the charcoal. The results on the rate of adsorption, time of desorption, and equilibrium adsorption agree closely among themselves, which makes it possible to make separate determinations of the rate constants for adsorption and desorption. By the same method, a study was made of the reaction of nitric oxide with oxygen on a charcoal surface.

The second rapid process investigated in the apparatus developed by the speaker was the reaction between chlorotriphenylmethane and ethyllithium. It was possible to follow the formation of a high concentration of triphenylmethyl radicals in the early stages of the process and the gradual fall in concentration to the equilibrium value.

Corresponding Member of the Academy S. Z. Roginsky and Academician M. M. Dubinin participated in the discussion of this paper.

A paper by V. I. Talroze, candidate of physical and mathematical sciences, was devoted to the question of charge transfer as a method to obtain mass spectra having one or only a few lines.

The speaker pointed out that the main fundamental difficulty in the modern mass-spectroscopic analysis of gas mixtures is associated with the method of electronic impulse used in the production of ions. In the bombardment of molecules with electrons of the usual energy (some tens of electron-volts), not only molecular ions, but also large amounts of ionic fragments, are formed, and the mass spectrum therefore contains many lines. As a result, the solution of many problems of analysis is rendered difficult, for example, the determination of small amounts of unsaturated hydrocarbons in saturated hydrocarbons and, particularly, the determination of low concentrations of free radicals in gas reactions. The author reported that he had proposed the use of the method of charge transfer from ions with energies of a few tens or hundreds of electron volts to the molecules of the mixture being analyzed so as to obtain mass spectra having one or only a few lines.

V. L. Talroze described some experiments in which hydrocarbons were ionized in this way. The bombarding ions were obtained by electron bombardment in a special ion gun and were then directed into the charge-transfer chamber, which served as the ion source of the mass spectrometer. It was found, for example, that for bombardment with carbon disulfide ions the sensitivity of the mass spectrometer toward propene was at least 25 times as great as its sensitivity toward propane. This is of importance not only for the analysis of hydrocarbon mixtures, but also for the determination of a free radical such as CH_3, the ionization potential of which is close to that of C_3H_6. Charge transfer to complex molecules has no sharply marked resonance character, which is of special importance for the application of the method.

Academician N. N. Semenov and Dr. V. V. Voevodsky participated in the discussion on this paper.

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Division of Chemical Sciences

IN ENGLISH TRANSLATION

August, 1957

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